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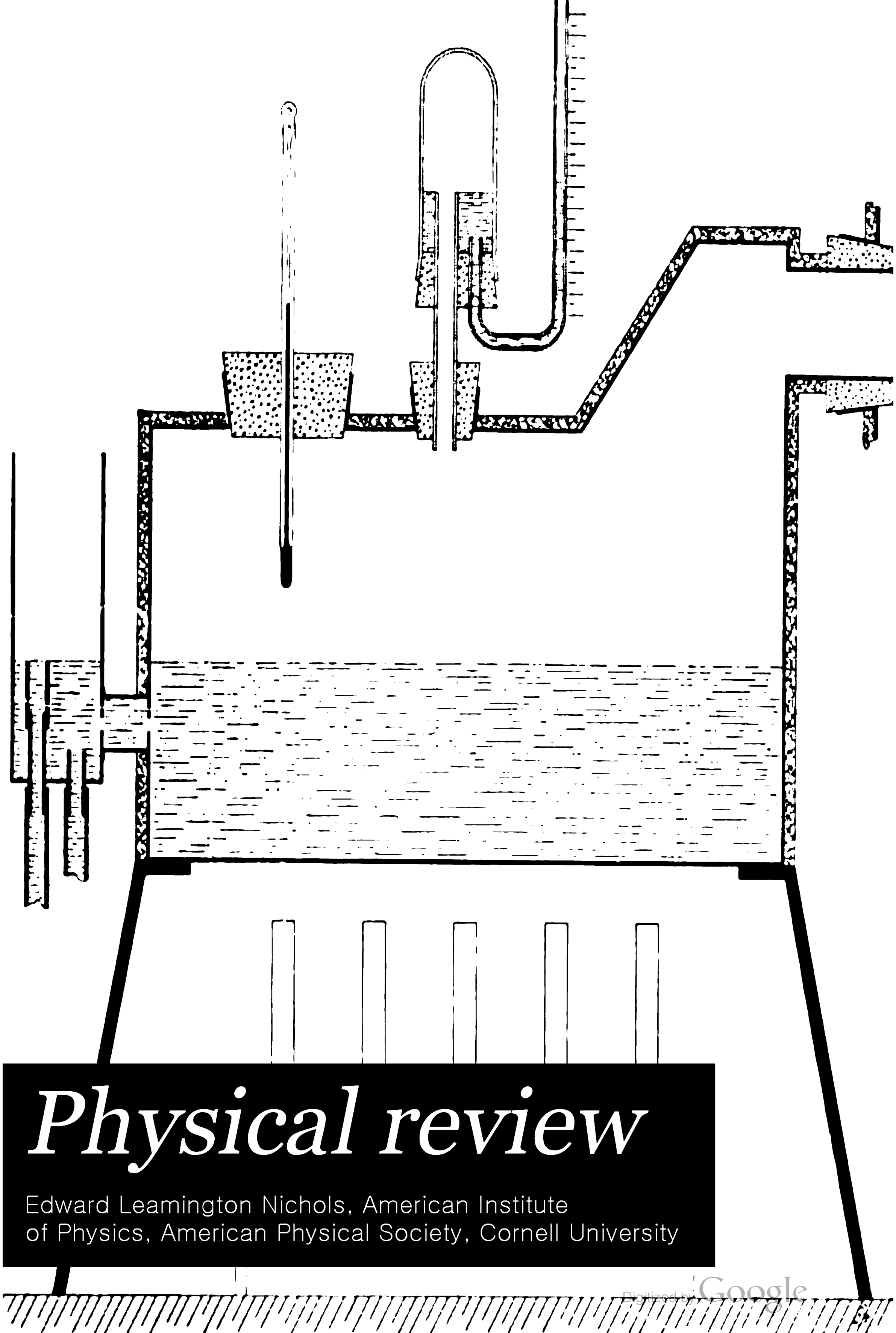

Physical review

Edward Leamington Nichols, American Institute of Physics, American Physical Society, Cornell University

THE
PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND
THEORETICAL PHYSICS

CONDUCTED WITH THE CO-OPERATION
OF THE
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BY
EDWARD L. NICHOLS, ERNEST MERRITT,
AND FREDERICK BEDELL

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THE

PHYSICAL REVIEW.

A STUDY OF THE RADIATIONS EMITTED BY A RIGHI VIBRATOR.

BY HARLEY R. WILLARD AND L. ELMER WOODMAN.

I. INTRODUCTION.

There are two views regarding the nature of the radiation emitted by a Hertz vibrator. Sarasin and de la Rive,[1] Garbasso,[2] and others,[3] interpreting their experiments, came to the conclusion that each vibrator sends out all wave-lengths within certain wide limits, and that each resonator picks out from these different vibrations the one corresponding to its own period. The name of "multiple resonance" was given to this phenomenon.

Poincaré,[4] Bjerkness,[5] and others[6] have a different view. They are of the opinion that each vibrator sends out only vibrations of a single period which are highly damped, and that the "multiple resonance" effects observed by Sarasin and de la Rive and others are due to the damped character of these vibrations. They support these views by theory and experiment.

---

[1] Sarasin and de la Rive, Compt. Rend., p. 439, 1892.

[2] Garbasso, Journal de Physique, Vol. 22, p. 259, 1893.

[3] Waitz, Wied. Ann., Vol. 41, p. 435–447; Geitler, Wied. Ann., Vol. 66, p. 999, 1898; Gutton, Journal de Physique, Dec. 1901, p. 752; Klemencic and Czermak, Wied. Ann., Vol. 50, p. 175; Trouton, Nature, Vol. 41, p. 295, 1890; Garbasso and Aschkinass, Wied. Ann., Vol. 53, p. 534; Swingedauw, Arch. des Sci. Phys. et Nat. de Geneve, Vol. 3, p. 476, 1897; St. John, Phil. Mag., Vol. 88, p. 425, 1894; Lamotte, Journal de Physique, Oct. 1901, p. 589.

[4] H. Poincaré, "Electricité et Optique," Vol. 2, p. 250.

[5] Bjerkness, Wied. Ann., Vol. 44, p. 92, 1891.

[6] Bose, Phil. Mag., Vol. 43, p. 55; Drude, Journal de Physique, Vol. 26, p. 643; Wied. Ann., Vol. 61, p. 631, 1897; Arch. des Sci. Phys. et Nat. de Geneve, Vol. 3, p. 554, 1897; Strindberg, Journal de Physique, Vol. 24, p. 142, 1895; Planck, Wied. Ann., Vol. 60, p. 577, 599, 1897; Decombe, Journal de Physique, Vol. 28, p. 450, 1899; Hertz, "Electric Waves."

The experiments described in this paper were undertaken for the purpose of determining: (*a*) the nature of the radiation emitted by a Righi vibrator; (*b*) the dependence of the length of a linear receiver upon the wave-length with which it is in resonance. This problem, however, resolved itself into: (1) the measurement of the energy received from the same vibrator by resonators of different lengths, and (2) the measurement of the wave-lengths obtained with different resonators.

II. The Apparatus.

The Vibrator. — Two Righi[1] vibrators were used in these experiments, one twice the linear dimensions of the other. The mounting and arrangement of parts is shown in Fig. 1. Spheres 3 and 4 were fastened to the glass rod *AB* by means of hard rubber rods, and to these spheres were attached the lead wires from the induction coil. Spheres 1 and 2 were supported in a glass cylinder filled with olive oil. This makes two spark-gaps at which the spark passes in air, and one at which the spark passes in oil. It is the

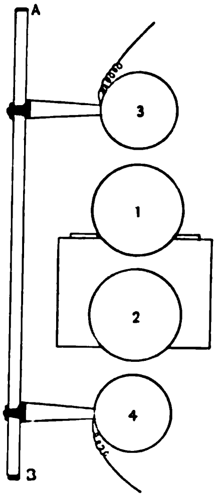

Fig. 1.

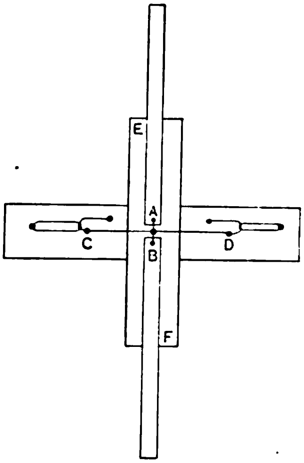

Fig. 2.

---

[1] Righi, Mem. del R. Acad. dei Sc. del Inst. di Bologna, T. IV. 1894.

latter discharge which sets up the train of waves studied in these experiments, although there seemed at times to be good reasons for thinking that the other discharges also caused wave trains which had more or less effect upon the receiver.

In the smaller vibrator the spheres 3 and 4 were 20 mm. in diameter and the spheres 1 and 2 were 25.4 mm. In the larger vibrator the diameter of the smaller spheres was 20 mm., and of the larger 50.8 mm. The large spheres had to be taken out and polished frequently because the energy of the vibrations fell off rapidly as the surface of the spheres at the spark-gap deteriorated.

The Receiver. — The receiver used was very similar to the Klemencic thermo-element used by A. D. Cole.[1] Fig. 2 shows the general construction of a thermo-junction, various modifications of which were used. Two strips of copper foil were fastened by means of shellac to two of the arms of a wooden cross *EF*. To one of the copper strips an iron wire 0.04 mm. in diameter was soldered, and to the other a constantan wire 0.107 mm. in diameter. At the middle of the gap, between the copper strips the wires were crossed and the ends soldered at *C* and *D* to copper wires leading to the galvanometer. The copper wires were carried back on each side through holes in the wooden cross, leaving loops through which rubber bands were passed. Good contact between the wires of the thermo-junction was obtained by keeping the rubber bands extended. The resistance of such a thermo-junction was about one ohm.

The Parabolic Mirrors. — The vibrator and receiver were each placed in the focal line of a cylindrical parabolic mirror. Two pairs of mirrors were used. With the vibrator having the 2.54 cm. spheres the mirrors were 30 cm. high by 38 cm. wide, and of 3.7 cm. focal length. The other mirrors used with the vibrator having the 5.08 cm. spheres were 64 cm. high by 90 cm. wide a the opening, and of 10 cm. focal length.

In the determination of the energy curves, given later, the length of the receiver was shortened between successive series of measurements. To accomplish this with the least jar or disturbance to the thermo-junction, the receiver was attached to a glass tube which passed through a hole in the back of the mirror and which carried the wires connecting the receiver to the galvanometer. The receiver could thus be easily removed, the ends shortened, and again replaced.

---

[1] A. D. Cole, Physical Review, Vol. IV., No. 19. July-August, 1896.

The Galvanometers. — The galvanometers were four-coil reflecting galvanometers of the Thomson type. The resistance of the four coils connected in multiple was five ohms. The sensitiveness of galvanometer A was 8×10^{-9} and of galvanometer B 4×10^{-9}, for a period of twelve seconds.

The arrangement of the apparatus in the first series of experiments is shown in Fig. 3. The two galvanometers are shown at A and B. The relative positions of the vibrator and receiver mirrors are at V and R. The distance between the vibrator and receiver was varied until the radiation falling on the receiver in the mirror R, gave a convenient working throw of galvanometer B. The induction coil was placed at I. The disturbing influence of the induction coil upon the galvanometers was reduced to a minimum by rotating the coil and a correction was added to the galvanometer deflections for the uneliminated disturbance, which was small. The circuits leading to the galvanometers were twisted to prevent any disturbance from induced currents.

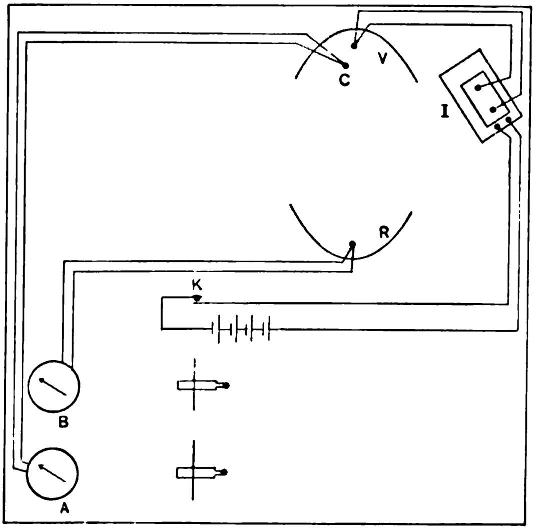

Fig. 3.

Accidental thermal disturbances were eliminated as far as possible by wrapping all connections in cotton and by placing sheets of cardboard over the apertures of the mirrors.

To eliminate variations in the intensity of the emission of the vibrator, the plan of Klemencic and Czermak[1] of a "control" receiver (*c*, Fig. 3) placed in the vibrator mirror was adopted. No change was made is this thermo-junction during any one series of readings. Its lead wires were attached to galvanometer *A*. In each set of readings the throws of both galvanometers were taken and the ratios of the two throws were very nearly constant for any one set of conditions. After taking these precautions the sets of readings were consistent in themselves, and also from day to day.

Before each series of measurements the two galvanometers were carefully adjusted to the same period. This adjustment under ordinary circumstances held for an hour or more without change, thus giving ample time for the determination of the ratios for any one receiver length. Before each observation conditions of quiet for both galvanometers were awaited. A key closing the primary circuit of the induction coil was then pressed and the vibrator held in operation until the end of the first throw of the galvanometers. The key was then opened and the turning point of the return throw observed. The difference between the scale reading of the turning point of the first throw and the mean of the zero position and turning point of the return swing was taken as the deflection. To the deflection thus obtained small corrections were added to eliminate the slight disturbing action of the induction coil upon the needle systems.

Ordinarily ten observations constituted a series and the mean of the ratios of the deflections of the two galvanometers determined the ratio for one length of the receiver. The note-book record of one such series is shown entire in Table I.

In this way ratios were obtained for different lengths of the receiver, varied by steps from 173 mm. to 16 mm. These ratios are exhibited in Table II. and plotted as an energy curve in No. 2, Fig. 4, in which receiver lengths are shown as abscissæ and ratios as ordinates.

This operation was repeated with three other receivers of varying widths and construction using the smaller vibrator, and also with three different receivers, using the larger vibrator as a source.

---

[1] Klemencic and Czermak, Wied. Ann., Vol. 50, p. 175.

Table I.

Feb. 27, 1902. *Period* 14.2 *sec.* *Length of Each Copper Strip* 14.5 *mm.*
Total Length of Thermo-Junction 32 *mm.*

Galvanometer A.					**Galvanometer B.**					
Return Swing.	**Zero.**	**First Turning Point.**	**Deflection.**	**Corrected Deflection.**	**Return Swing.**	**Zero.**	**First Turning Point.**	**Deflection.**	**Corrected Deflection.**	**Ratio of Deflections.**
25.75	29.05	33.45	6.05	5.68	20.00	20.80	22.40	2.00	1.92	.338
25.95	29.05	33.35	5.85	5.48	20.05	20.80	22.40	1.97	1.89	.345
25.95	29.24	33.65	6.05	5.68	20.04	20.80	22.50	2.08	2.00	.352
26.00	29.38	33.95	6.26	5.89	19.97	20.80	22.50	2.11	2.03	.345
25.70	29.70	34.95	7.25	6.88	19.80	20.78	22.74	2.45	2.37	.344
26.35	29.90	34.65	6.52	6.15	19.65	20.50	22.25	2.17	2.09	.340
26.65	30.35	35.30	6.80	6.43	19.14	20.10	22.00	2.38	2.30	.358
26.70	30.62	35.90	7.24	6.87	18.80	19.80	21.80	2.50	2.42	.352
26.85	30.66	35.85	7.09	6.72	18.84	19.82	21.80	2.47	2.39	.356
27.35	30.90	35.65	6.52	6.15	18.84	19.70	21.50	2.23	2.15	.350
27.35	31.10	36.10	6.87	6.50	18.68	19.60	21.48	2.34	2.26	.348
									Mean	.348

Table II.

Total Length of Resonator.	**Ratio $\frac{\text{Galv. B.}}{\text{Galv. A.}}$**	**Total Length of Resonator.**	**Ratio $\frac{\text{Galv. B.}}{\text{Galv. A.}}$**	**Total Length of Resonator.**	**Ratio $\frac{\text{Galv. B.}}{\text{Galv. A.}}$**
173	.366	77	.972	31	.263
161	.382	73	.882	29	.307
152	.386	59	.603	27	.241
142	.408	49	.476	25	.211
133	.438	45	.434	23	.212
113	.570	43	.400	21	.140
93	.883	41	.360	19	.144
89	.922	39	.375	17	.165
85	1.003	37	.297	16	.073
81	1.022	33	.298		

Discussion of the Energy Curves. — The curves 1 to 4, Fig. 4, were obtained by using the smaller vibrator, operated by a 10 cm. spark length induction coil driven by four storage cells. The receiver and vibrator were 152 cm. apart. The same "control" receiver (*c*. Fig. 3) was used for the four curves. The copper strips on this thermo-junction were each 4.4 mm. wide and 30 mm. long. The space between the two copper strips was 2 mm., making the total receiver length equal to 62 mm. The small iron and constantan wires were soldered at the junction so that no tension was required to insure contact. This "control" receiver was placed 9 cm. in front of the spark gap of the vibrator.

The characteristic points on energy curves 1, 2, 3 and 4 are shown in Table III. with specifications of the receiver used in each case.

Table III.

	No. 1.	No. 2.	No. 3.	No. 4.	Mean.
Width of resonator strips.	4.6 mm.	4.6 mm.	No. 18 Cu wire.	3 mm.	
Length of fine wire connecting resonator halves.	3 mm.	3 mm.	1.6 mm.	2.3 mm.	
First maximum.	80.0 ?	82.5	81.5	80.5 ?	81.1
Second "	41.5	39.0	41.5	40.2	40.55
Third "		29.0	26.0 ?	29.0 ?	28.0
Additional maxima.					
1.			51.9	56.5	54.2
2.		17.0		18.0 ?	17.5
3.				70.2	70.2

As the ratio of width to length in the shortened receivers was relatively large, receivers of different widths were studied to discover any effect upon the energy curves traceable to a greater or less constriction of the stream lines traversing the thermo-junction.

The curves apparently show either an emission of the vibrator corresponding to a damped fundamental vibration with one, two, or three less clearly-marked maxima, some of which stand in nearly the same numerical relation to the fundamental as upper partial vibrations in a stretched string; or the emission of a continuous spectrum with accented fundamental and upper partial vibrations. The former interpretation corresponds to the conclusions drawn by Bjerkness, Poincaré and others, and the latter to the views of Sarasin and de la Rive and their followers. So far as the writers are aware, none of the above investigators took any account of upper partial vibrations.

In the first curve a fundamental and the first upper partial not very clearly marked appear. The thermo-junction was accidentally

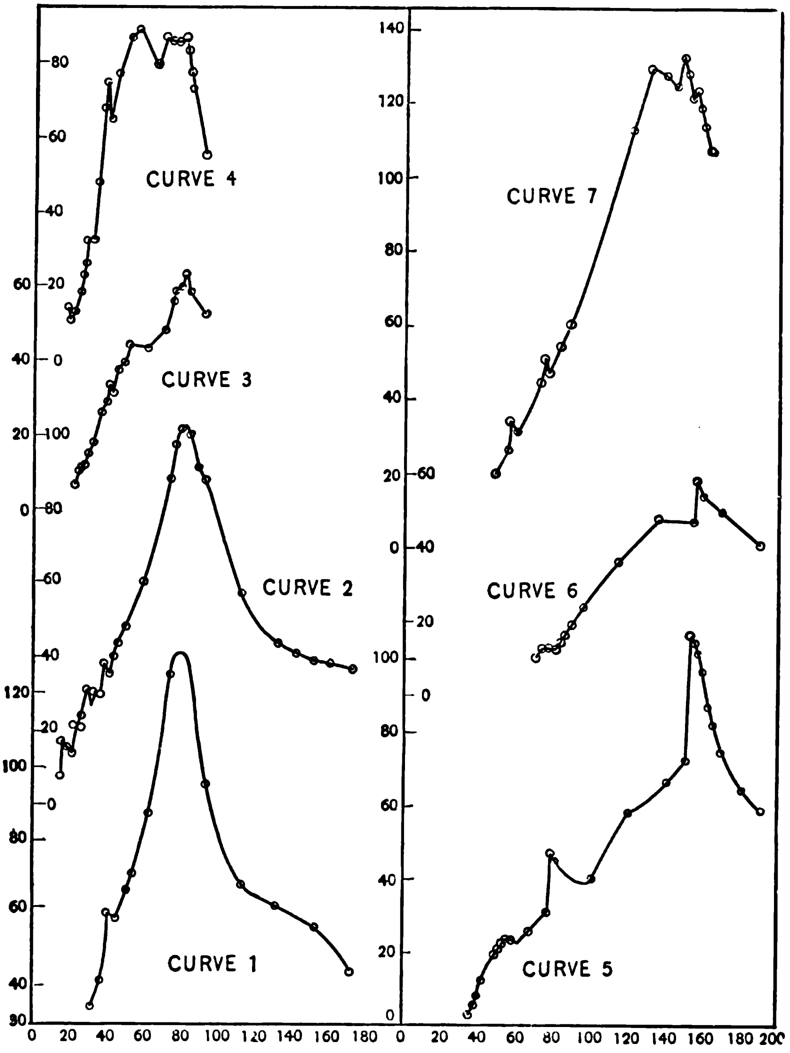

Fig. 4.

broken in the process of shortening the receiver just before the length corresponding to the second upper partial was reached. So few points were observed on this curve in the region of the maximum corresponding to the fundamental vibration as to leave the receiver length corresponding to this maximum somewhat in doubt.

The second curve was the most characteristic one secured. It shows a well-defined maximum corresponding to a fundamental and two fairly distinct maxima corresponding to the first two upper partials.

In curve 3 the course of the energy curve is less regular, but the fundamental and first two upper partial maxima appear. For a receiver length of about 26 mm. a doubtful maximum occurs.

Curve 4 is the least satisfactory of the group in that the fundamental maximum appears to be very complex and not sharply defined. At the point corresponding to what has been called the first upper partial on the foregoing curves, a well-defined maximum appears. At the position corresponding to the second upper partial in curve 2, there is only a slight kink in the curve. At a receiver length of 18 mm. indications of an additional maximum appear, but the thermo-junction was unfortunately broken in handling before its position was defined. It resembles, however, in position the last maximum on curve 2, which is not far from the position for a third upper partial.

Curves 3 and 4 show maxima at one or two other points in their length, which are recorded in the table as additional maxima.

In order to see if there was any simple linear relation between the length of receiver giving the fundamental maximum and the diameter of the larger spheres in the vibrator, energy curves 5, 6 and 7 were obtained in the same manner, but using a vibrator in which the diameter of the larger spheres was twice as great. For curves 5 and 6 the vibrator was operated by the same induction coil as for the first four curves. The "control" receiver (*c*. Fig. 3) was made of copper strips 4 mm. wide, with a space of 1.5 mm. between them, making the total length of the receiver 163.5 mm. It was placed 18 cm. in front of the spark gap. The distance between the focal lines of the parabolic mirrors was 187 cm. for curve 5 and 150 cm. for curve 6. For curve 7, a 20-cm. spark-gap induction coil driven by 21 storage cells was used. It was placed in another room about 110 feet from the vibrator and rotated so as to reduce to a minimum the magnetic effect upon the galvanometers.

The "control" receiver was cut down to 158 mm. and the vibrator and receiver were placed 273 cm. apart.

Table IV. gives the dimensions and details of construction of the three thermo-junctions used and also the total receiver lengths corresponding to the maxima on the three curves.

Curve 5 shows a very distinct fundamental and two upper partials. The maximum of the second upper partial is so broad that it is difficult to determine just what receiver length would correspond to it, but the first upper partial gives a very distinct maximum on the curve.

TABLE IV.

	No. 5.	No. 6.	No. 7.	Mean.
Width of resonator strips.	4 mm.	4 mm.	4 mm.	
Length of fine wire connecting resonator halves.	2 "	2 "	1.7 "	
1st Maximum.	154	158	156?	156.0
2d "	80	79?	76	78.3
3rd "	56?		58	57.0
Additional Maxima.				
1.			148	148
2.			131	131

Curve 6 shows a sharp maximum for the fundamental, and one upper partial, not so clearly marked as the corresponding one in curve 5.

Curve 7 is more complex around the fundamental than either of the other two. By comparing it with curves 5 and 6 it seems that the slight elevation on the right side of the curve may be the fundamental but the evidence is not convincing. There are, however, two upper partials present which correspond very closely with the upper partials of curve 5. In this curve there are two additional maxima which seem to have no simple relation to the assumed fundamental, and two upper partials.

A study of these three curves, as well as of the four curves obtained with the smaller vibrator, seems to show that the fundamental radiation sent out by a Righi vibrator becomes more complex the longer the vibrator is used in spite of the fact that the surfaces in oil were frequently repolished.

The smaller secondary maxima occur upon the steeply descending sides of the general energy curve and it might therefore be expected that some displacement toward the side of a longer receiver should be looked for. Although this might explain the apparent displacement of the second upper partial in the longer vibrator, no plain evidence of it can be detected in the corresponding upper partial of the smaller vibrator. On the other hand, the shorter receiver actually takes up less energy than a longer receiver. If the energy readings are divided by the length of the receiver, the curve would not fall so rapidly and the observed maxima would be displaced toward the shorter lengths and would be more pronounced. Other conditions which might alter the position of maxima on the curves are :

First, the resistance in the thermo-junction of the receiver might be changed by a jar or strain in clipping off the ends between two series. The greatest care possible was exercised in this process to avoid any shocks or strains which might produce such a change of resistance.

Second, any change or deterioration in the spark gap of the vibrator producing a change in its emission might not affect both receivers in the same degree.

Third, in comparing the receiver lengths for the fundamental and upper partial vibrations, it must be borne in mind that the ratios of width to length of the receivers were very different for the different lengths.

It is very probable that the results obtained in these experiments are not due to the vibrator alone, but rather to the combined action of vibrator and receiver. The fact that the curves all show a fundamental and one or more upper partials when the receiver was changed and the vibrator was kept the same, seems to show that the form of the curve was determined more by the characteristics of the vibrator than by those of the receiver.

While the experimental data is insufficient to warrant rigid conclusions, it is worthy of notice that the ratio of the diameters of the large spheres in the two vibrators is very nearly equal to the ratio of the receiver lengths which correspond to the fundamentals, as determined from the energy curves. The work with the interferometer, which is given in the next section, was taken up to determine whether the same ratio would hold between the fundamental wave-lengths emitted by the two vibrators.

III. INTERFEROMETER FOR MEASURING WAVE-LENGTHS.

In measuring the wave-length of our vibrations, we made use of the interferometer, as arranged by G. F. Hull,[1] in 1896. A description of the instrument will be given below. The interferometer seemed best for our use. In the Quincke tube arrangement, λ has been found by Drude to depend upon the diameter of the tube. On this account the Quincke tube was not adapted to the conditions of our experiment.

The relatively long path between receiver and vibrator in the Boltzmann mirrors and the shadowing of one mirror by the other, cause a diminution of energy and give poor conditions for interference. There is no such shadowing in the interferometer, and the distances can be made relatively small without affecting the success of the experiment. The plan of the interferometer is shown in Fig. 5.

The mirrors *V* and *R*, containing the vibrator and receiver, are those described in Part II. M_1 and M_2 are plane mirrors for reflecting the waves at normal incidence. They were constructed of wood and covered with tin foil. When the smaller vibrator was used, these mirrors were 51 cm. long by 38 cm. high. When the larger vibrator was used, the mirrors were 111 cm. long by 70 cm. high. Difference of path was obtained by the movement of M_2 along the ways *T*, and distances were measured by means of the scale *W*. The separating surface[2] *S* was made of strips of tin one cm. wide and of varying lengths so that the whole separating sur-

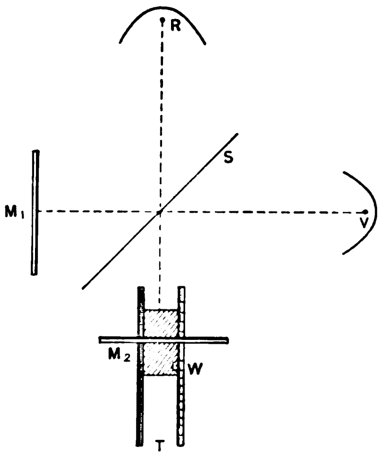

Fig. 5.

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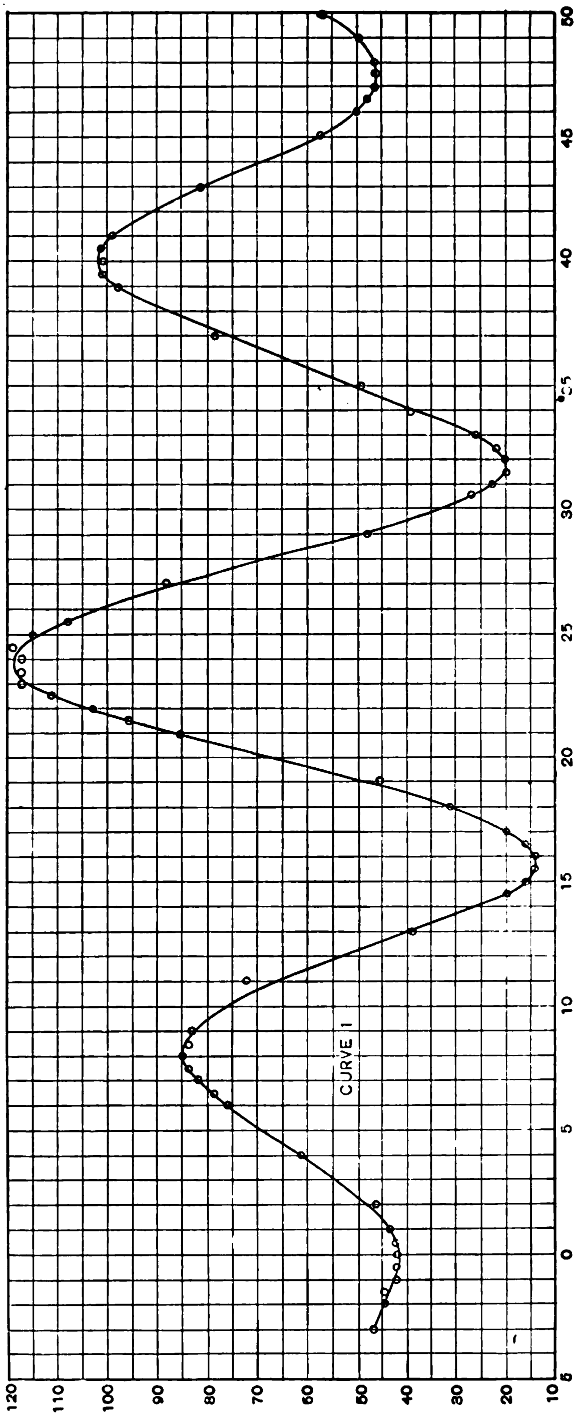
[1] G. F. Hull, PHYSICAL REVIEW, Vol. 28, 1897.

[2] G F. Hull, l. c.


CURVE I
120
110
100
90
80
70
60
50
40
30
20
10
-5
0
5
10
15
20
25
30
35
40
45
50

face would not be in resonance with any particular wave-length. They were hung over an iron rod and were held in one plane at the bottom by a strip of wood. The grating space — the distance between the centers of the strips — was changed for each receiver to secure equality between transmission and reflection. To determine the grating space, the mirrors M_1 and M_2 were removed, and the positions of the tin strips were adjusted until the energy reflected from the grating was equal to the energy transmitted. A graduated force table was used for measuring angles.

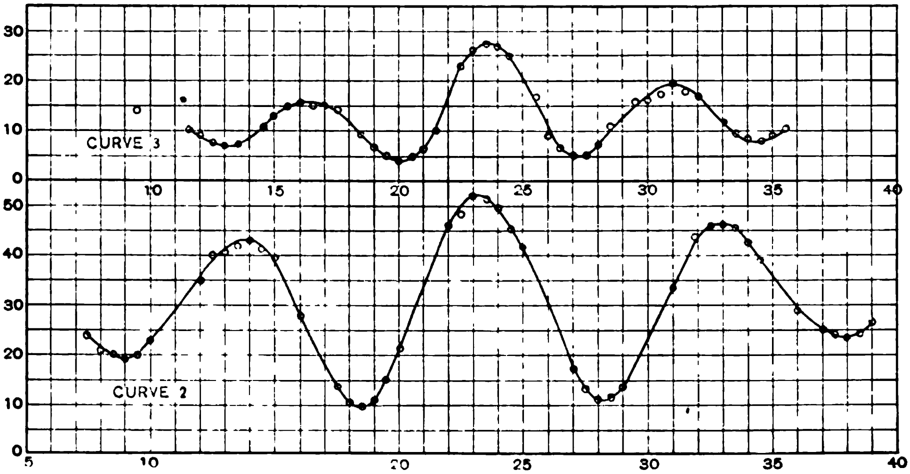


Fig. 7.

In curve 1, Fig. 6, it was found that the condition for equal reflection and transmission was obtained when the grating space was equal to 12 cm.; in curves 2, 3 and 4, Figs. 7 and 8, when it was equal to 8 cm., 6 cm. and 8.9 cm., respectively.

When the grating space had been determined for each vibrator and receiver, the vibrator was placed in its mirror and a resonator of the required dimensions was constructed and placed in the focal line of the receiving mirror. The mirrors were then arranged as indicated in Fig. 5.

The frequent repolishing of the vibrator spheres usually did not affect the ratios of the two galvanometer throws, but sometimes it caused a deviation of a few per cent. which resulted in an upward

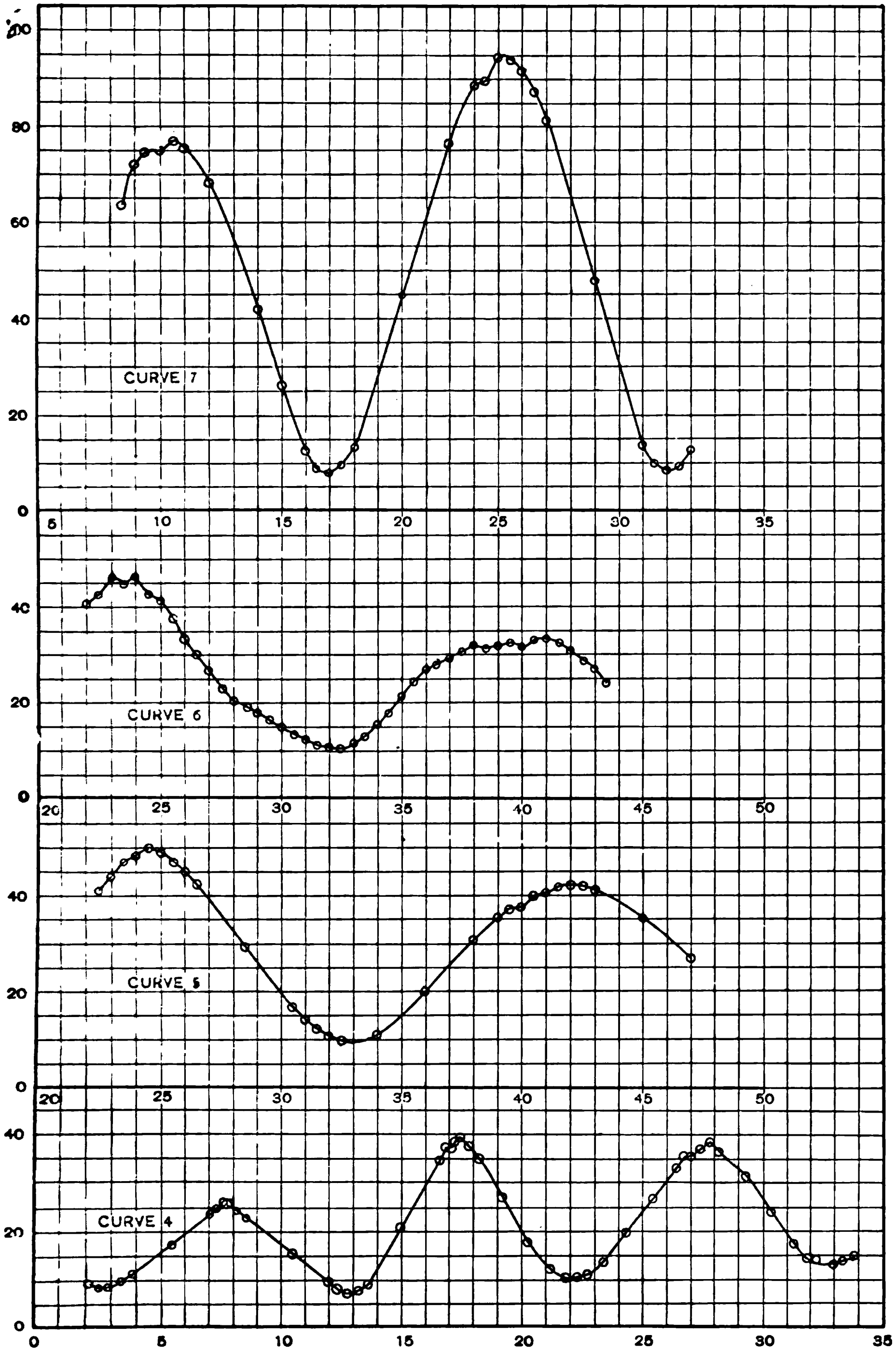

100
80
60
40
20
0
CURVE 7
5
10
15
20
25
30
35
40
20
0
CURVE 6
20
25
30
35
40
45
50
40
20
0
CURVE 5
20
25
30
35
40
45
50
40
20
0
CURVE 4
0
5
10
15
20
25
30
35

Fig. 8.

or downward displacement of the interference curve. The vibrator was never disturbed while working in the regions of the maxima and minima, so that any variation of ratio would not affect the value of the wave-length.

The Measurement of Wave-lengths. — The measurement of the wave-length consisted in taking readings for different positions of the movable mirror, going through the whole curve and retracing the path, and from these readings in plotting an interference curve. The curve consisted of well-marked maxima and minima, and the distance between two maxima or two minima was equal to one half wave-length of the vibration. The readings on the scale of the movable mirror were used as abscissæ of the curve and the ratios of the two galvanometer readings as ordinates. The method of taking the readings was as follows:

Starting with no difference of path, readings were taken in order through the different maxima and minima of the curve. Near the maxima and minima the readings were taken very close together, in order definitely to determine these points. At a maximum or minimum, two readings were taken every few millimeters on both sides and around these parts of the curve. In this way the curve was gone over three times, and at least six readings were taken at every point, the mean of these readings being the value plotted. This was done to eliminate as far as possible the influence of irregularities in the action of the vibrator and galvanometer, and in external conditions. At intermediate points of the curve, three or four readings were taken at intervals of one or two centimeters. In this way the interference curves were obtained, and the positions of three maxima and four minima in each curve were determined.

In the case of the smaller spheres, only the wave-length of the fundamental vibration was measured; for it was thought that there would not be enough energy to make accurate measurement possible in the upper partial vibrations. In the larger vibrator the wave-lengths of the fundamental and two upper partials were sought. The wave-lengths as determined by the interference curves are given in Table V.

Non-Effect of Grating Space on λ. — It was not known whether the grating space exerted any influence on the wave-length. Two series of measurements were therefore made to determine what this effect was. Curves 5 and 6, Fig. 8, show the results of this work. Only a portion of the interference curve was obtained in each case; for since the difference in grating space was taken between such wide limits, it was thought that a few points of the curve would show whether the grating space had any appreciable effect on the wave-length. The curves are very irregular, and the maxima and minima points at best can be only roughly decided upon. In curve 5, the grating space was 17 cm. and in curve 6, it was 6 cm. In both curves the thermo-junction had a length of 15.8 cm. Curve 5 gives a wave-length equal to 34.8 cm., and curve 6 gives one equal to 33.6 cm. Both of the wave-lengths measured from these curves are greater than the wave length of the fundamental vibration, and the difference between them and the fundamental is a little more than the outside limits of error. The deviation from the fundamental may be accounted for by the fact that there is more scattered radiation when the grating space is not adjusted for equal reflection and transmission, consequently the maxima and minima are less distinct, as will be seen from curves 5 and 6, and λ is harder to measure.

TABLE V.

Large Vibrator.						Small Vibrator.	
Fundamental. Curve 1.		First Upper Partial. Curve 2.		Second Upper Partial. Curve 3.		Fundamental. Curve 4.	
1/4λ.	1/2λ.	1/4λ.	1/2λ.	1/4λ.	1/2λ.	1/4λ.	1/2λ.
8.25		4.85		3.40		5.00	
7.60	15.85	4.60	9.45	3.50	6.90	5.30	10.30
8.20	15.80	4.65	9.25	3.65	7.15	4.40	9.70
7.85	16.05	5.10	9.75	3.55	7.20	4.85	9.25
8.35	16.20	4.75	9.85	3.80	7.35	5.60	10.45
7.50	15.85	5.00	9.75	3.30	7.10	4.80	10.40
Mean	15.95		9.61		7.14		10.02
Mean error = 0.9%			2.2 %		1.6 %		4.4 %
Prob. error = 0.3%			0.8 %		0.7 %		1.6 %
$\lambda = 31.90$ cm.		$\lambda = 19.22$ cm.		$\lambda = 14.28$ cm.		$\lambda = 20.04$ cm.	

If the grating space had exerted any decided influence on the wave length, we might have expected that the wave-length determined by curve 6 would have been smaller than the fundamental, which had a grating space of 12 cm., and that the wave-length determined by curve 5 would have been greater. As these effects were not found it appears that the grating space alone has no appreciable effect on the wave-length measured.

Measurement of λ by a receiver not in resonance with the vibrator. — It was desired to determine the wave-length measured by a receiver whose dimensions were between those of the receiver for the fundamental and the receiver for the first upper partial. The experiment was performed with a resonator 118 mm. long, and an interference curve, No. 7, was plotted. The wave-length taken from this curve was equal to 27.4 cm. This value differs very widely from the wave-length of the fundamental and still more widely from that of the first harmonic. The following question now arises. Is this divergence due to the shorter length of the receiver and therefore does it tend to confirm the theory that the receiver determines the length of the wave measured, or does it show that there are waves present other than the fundamental and its series of upper partials? These experiments are not complete enough to answer this question conclusively. A study of the energy curves will show that in several cases the principal maximum is very irregular and this would seem to indicate that there is, mixed up with the fundamental, other vibrations of nearly its own period. Some of the maxima on the interference curves show irregularities which would indicate the same. In curve 7, Fig. 4, appear supplementary maxima at 148 and 131 on the scale, and the wave-length measured with this receiver very nearly corresponds to the latter vibration, supposing for the time that wave-length bears a constant ratio to receiver-length. This length of receiver was chosen entirely at random, and it is unfortunate that this precise length was taken, for under the circumstances it is not possible to answer definitely the foregoing question.

It was thought at first that with the interferometer it would be possible to measure absolutely the length of electric vibrations if some receiver could be found which had no definite period of its own. G. F. Hull[1] used a coherer for a receiver in his work with the interferometer and he found that even this receiver influenced to some extent the wave-length measured. The electric vibration emitted by such an exciter as was used here is heavily damped, and though the damping as shown by the interference curves is less than theory suggests,[1] yet in such a vibration the first pulse is relatively more effective than the waves which follow it.

When the first pulse of the damped wave train strikes the receiver, the resonator is set in vibration and it continues to vibrate with its own period. This vibration of the receiver is stopped only when the mirrors of the interferometer are in such a position as to cause the waves to arrive in a phase opposite to the vibration of the receiver. Thus there is measured the wave-length of the vibrator as modified by the receiver and not the absolute length of the wave sent out by the vibrator.

Relation Between Resonator-length and Wave-length. — It is interesting to note the dependence of the resonator-length upon the wave-length, as shown from these experiments, and to determine whether in this respect the results of these experiments agree with the values found by other investigators. Poincaré[2] gives 2 as the ratio of wave-length to resonator-length. Macdonald[3] theoretically derives the formula $\lambda = Kl$, where λ is the wave-length, l the resonator-length, and K a constant. For the fundamental vibration, K in the formula $\lambda = Kl$, is equal to 2.53. This value has been proved to hold for circular receivers. Below is a table of values for K computed from these experiments:

	l	λ	$k = \frac{\lambda}{l}$
Small spheres, fundamental.	8.16	20.04	2.46
Large " "	15.8	31.90	2.02
first harmonic.	7.9	19.22	2.43
second "	5.6	14.28	2.55

It is evident that these values do not agree with the value given by Poincaré, but they agree approximately with the value given by Macdonald, except in the case of the fundamental for the larger spheres. Here K is equal to 2.02, while Macdonald's theory gives

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[1] G. F. Hull, l. c.

[2] Poincaré, "Les Oscillations Electriques."

[3] Macdonald, "Elective Waves," Adams Prize Essay in the Univ. of Cambridge, p. 111.

2.53. It looks as though the vibration between the small spheres and the large ones affects the fundamental in the case of this vibrator. But the harmonics may not be so affected and their λ's fall in with Macdonald's value. The same reasoning may account for the ragged energy curves in the region of the fundamental.

Basing the calculation on these experiments, it would seem that for a linear receiver the formula $\lambda = K(l + a)$, where λ is the wave-length, l the resonator-length, and K and a are constants, is more nearly correct than the formula $\lambda = Kl$. Using $K = 1.75$ and $a = 2.67$, the formula gives values for the different wave-lengths approximately equal to the experimental values. This can best be seen from a table.

Given $\lambda = K(l + a)$. $K = 1.75$. $a = 2.67$.

	Expt. Value.	Computed Value.
Small spheres, fundamental.	20.0	19.0
Large " "	31.9	32.3
first harmonic.	19.2	18.5
second "	14.3	14.47

Fundamental and Upper Partials.—A study of the table will show that, although the fundamental resonator for the larger spheres is approximately twice the length of the fundamental resonator for the smaller spheres, the wave-lengths do not have this simple relation. Nor do the wave-lengths of the upper partials of the larger spheres bear the same relation to the fundamental that the receivers for the upper partials bear to the receiver of the fundamental. But the wave-length of the fundamental of the smaller spheres is nearly equal to the wave-length of the first upper partial of the larger spheres. The receivers used to measure the wave-lengths of the vibrations were of the same length as the receivers found by the energy curves to be in resonance with the fundamental and upper partials of the exciter. These lengths have been said to bear nearly the same relation to each other as the upper partials bear to the fundamental in the vibration of a stretched string. The fact that the wave-lengths measured do not have this submultiple relation does not prove that the upper partial vibrations are not present. It is evident that this part of the experiment is not conclusive, but that it bears out the inference deduced in Part II., that a Righi vibrator sends out a fundamental and at least two upper partials.

Corrections Which May Be Applied to the Inference Curve. — If one of the mirrors of the interferometer is removed, it is found that the intensity of radiation falling upon the receiver is not a constant, as the position of the other mirror is changed. Indeed the intensity does not even decrease uniformly as the mirror is moved away from the separating surface, *i. e.*, as the path is increased, but there is a rise and fall in the intensity showing the influence of standing waves. The interference curve is therefore affected by those standing waves and also by scattered radiation. But the effects are small and do not alter the main argument.

IV. CONCLUSION.

The points brought out by these experiments are these:

1. That the measurement of energy with a linear receiver of definite length showed the existance of a fundamental and upper partials.

2. That the relation of the receiver-lengths for the fundamental and the successive upper partials stand in the relation 1, 2, 3.

3. That the wave-length and receiver-length are connected by the relation indicated in the formula $\lambda = K(l + a)$.

4. That the interference curves show that the damping in a Righi vibrator is less than the theoretical value computed by Thomson for the radiation from a single sphere.

5. That the grating space of the separating surface does not affect the wave-length measured.

6. The character of the emission of a Righi vibrator, as shown by the foregoing experiments, may be accounted for by a modified statement of Sarasin and de la Rive's hypothesis, but is more rationally explained, in the opinion of the writers, on the basis of the hypothesis of Bjerkness and Poincaré. The results of the present experiments are, however, too limited in extent and too uncertain to give conclusive evidence in favor of either view.

A portion of this paper was submitted by the writers to the faculty of Dartmouth College as a thesis for the degree of Master of Arts.

These experiments were performed in the Wilder Physical Laboratory in Dartmouth College under the direction of Prof. E. F. Nichols and Prof. G. F. Hull, to whom we are much indebted for many valuable suggestions both in the construction of apparatus and in the methods employed in the experiment.

ON THE THEORY OF THE ELECTROLYTIC RECTIFIER.

BY S. R. COOK.

WHEN aluminum, with a free metallic surface, is the anode of an electrolytic cell which has dilute sulphuric acid, aluminum sulphate, potassium aluminum sulphate (alum), ammonium aluminum sulphate, potassium cyanide, or potassium ferrocyanide for the electrolyte, there is quickly introduced into the electrolytic cell a condition which produces a very high apparent resistance, so long as the voltage is not above a certain critical value. If, however, the aluminum is made the kathode, in any of the above solutions, and carbon or platinum the anode, the cell becomes a very good electrolytic conductor. This anomalous action of the aluminum anode in an electrolytic cell, in which oxygen is one of the products of electrolysis, was observed in 1857 by Buff,[1] while making more detailed observation on Wheatstone's[2] experiments for determining the position of aluminum in the voltaic series. Buff found that when dilute sulphuric acid was the electrolyte, a dark skin appeared on the surface of the aluminum anode and that the resistance was very much greater than when the aluminum was the kathode and either carbon or platinum was the anode.

In 1869, Thomson's electrometer being accessible for the measurement of potential, independent of resistance; Tait[3] while measuring the polarization of several cells determined the polarization of aluminum in dilute sulphuric acid. He applied an electromotive force of six Grove cells (10.44 Daniels) and with the Thomson electrometer found a counter electromotive force of 5.20 Daniels. No explanation was given for this very high counter E.M.F. and until very recently no explanation has been offered for the very high apparent resistance of the aluminum anode.

[1] Buff, Liebig's Annalen, CII., p. 169, 1857.

[2] Phil. Mag. (4), X., p. 143, 1854.

[3] Phil. Mag. (4), XXXVIII., p. 243, 1869.

In 1877 Beetz[1] investigated the dark skin observed by Buff and concluded that it was the normal oxide or hydroxide. While Lawrie,[2] from the effect of amalgamation on the electrochemical behavior of aluminum, came to the conclusion that the action of the aluminum anode was due to an oxide or suboxide. Oberbeck[3] and Streintz[4] considered the film formed on the aluminum anode a non-conductor and suggested that the aluminum, non-conducting film, and solution formed a condenser. They found that this cell had a measurable capacity, and a condenser consisting of two aluminum plates in dilute sulphuric acid has been described by Haagn.[5] In 1897 it was shown by Pollak[6] and independently by Gratz[7] that a cell composed of aluminum and carbon or aluminum and platinum with dilute sulphuric acid as the electrolyte could be employed to rectify an alternating current. This discovery brought the cell into practical importance and in 1898 the efficiency of this electrolytic rectifier was investigated by Wilson.[8]

Norden[9] investigating the chemical composition of the film on the aluminum anode, came to the conclusion that with dilute sulphuric acid as the electrolyte the film was composed of the normal aluminum hydroxide $Al_2(OH)_6$ with some aluminum sulphate. Wilson has shown that this film of oxide or hydroxide formed on the aluminum anode has a very high resistance; having observed values up to 10,000 ohms. Norden[10] attempted an explanation of the cause of the high anodic resistance of aluminum. From observations he found that the resistance of the resting cell was much less than the active cell and also that the film (supposed aluminum hydroxide) was acted upon by the solution and he concluded that if the film was weakened by the dissolution action of the liquid bathing it while resting, the same action would take place in the active cell and the current would break through these weakened parts. Burgess and Hambuecher,[1] following the same general theory, tried to establish the existence of these small areas of disruption by removing the aluminum anode and depositing copper from a solution of copper sulphate in the openings made by the dissolution of the film. This theory, namely, that the high apparent resistance of the cell, when aluminum is the anode and low resistance when aluminum is the kathode, is due to the high ohmic resistance of the film which by disruption or dissolution action allows the current to flow through uninterrupted in one direction and closes up and almost completely prevents the passage of the current in the other direction, will be discussed later in connection with the data here presented.

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[1] Pogg. Annalen, Vol. CXXVII., p. 45; Vol. CLVI., p. 464.

[2] Phil. Mag. (5), XXII., p. 213, 1886.

[3] Wied. Annalen, XIX., p. 625, 1883.

[4] Wied. Annalen, XXXII., p. 116, 1887; XXXIV., p. 751, 1888.

[5] Zeit. für Electrochemie, III., p. 470, 1896-1897.

[6] Compt. Rend., CXXIV., p. 1443, 1897.

[7] Weid. Annalen, LXII., p. 323, 1879.

[8] Electrical Review (London), p. 371, 1898; Pro. Royal Society, Vol. LXIII., p. 329, 1898.

[9] Zeit. für Electrochemie VI., pp. 159, 188, 1899-1900.

[10] Elec. World and Eng., Vol. 38, p. 681, Oct. 26, 1901.

Dr. Guthe[2] in a paper read before the American Association for the Advancement of Science, at its Pittsburg meeting, advanced another theory for the explanation of the resistance of the aluminum anode. From experiments performed he concluded that the resistance was due to a film of gas, probably oxygen, at the anode, which, when the current was reversed, united with hydrogen or was dissolved in the solution. This theory will be reverted to again after the presentation of the data.

Taylor and Inglis in the Philosophical Magazine of March, 1903, have also suggested a theory of the aluminum anode. They have shown that by adding salts, containing negative ions, which would normally dissolve the anode, to the dilute sulphuric acid solution, the high resistance at the aluminum anode was prevented or destroyed. The theory advanced is that the high resistance is due to the property of the film of hydroxide to allow all ions except the SO_4 ions to pass through.

In view of the fact that Tait had, by a method independent of the resistance, obtained a counter electromotive force greater than is usual in electrolytic cells, and in view of the fact that the theories heretofore advanced to explain the apparent high resistance of the aluminum anode are not without objection, it seemed possible that, by a closer investigation of the value of the counter electromotive force, some further explanation of the high anodic resistance of the aluminum cell might reveal itself.

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[1] Trans. Amer. Elec. Chemical Soc., Vol. I., p. 147, 1902.

[2] Physical Review, Vol. XV., p. 327, 1903.

2. *Apparatus.*—The apparatus for the investigation of the counter electromotive force of the electrolytic rectifier consisted of an accumulator of twenty-eight cells, the electrolytic rectifier, which consisted of a cell with an aluminum plate, 7.5 x 10.2 cm., and a carbon plate of the same cross-sectional area, in a solution of potassium aluminum sulphate, a Weston ammeter, milliammeter and voltmeter, a relay and several keys and pole-changers arranged as in Fig. 1.

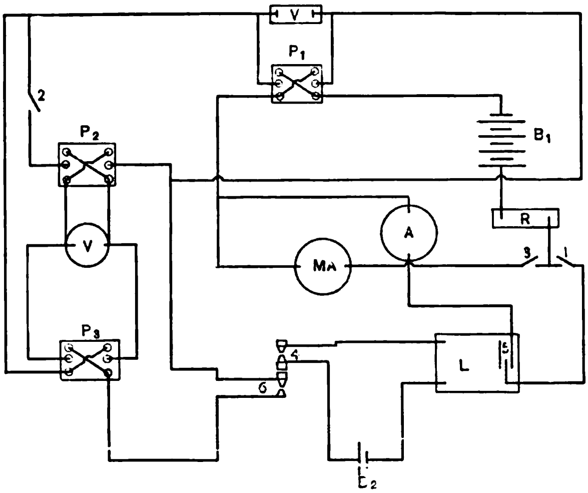

Fig. 1. Apparatus Diagram.

In the diagram V is the electrolytic rectifier, B_1 the accumulator, R a rheostat, L the relay, A and MA are the ammeter and milliammeter respectively, and V is the voltmeter. The pole-changers are designated by p_1, p_2, etc., and the keys by the numbers 1, 2, 3, etc., No. 5 being the break key on the relay, which was operated by the auxiliary battery B_2.

3. *The Method of Making the Observations.*—All connections having been made the plates were set at a distance of about 2 cm. and the electrolyzing current made by closing keys 1 and 5. The electrolyzing current now flows through the relay, the ammeter and the

electrolytic cell. The applied electromotive force is measured by closing key 2, thus putting the voltmeter across the terminals of the cell. The current flowing through the cell, when small, was measured by opening key 1 and closing key 3, thus putting the milliammeter in the circuit. When key 3 was opened key 1 was closed and remained closed throughout the remaining time for each observation. In order to measure the counter electromotive force, key 2 being open, key 4 was closed. The action of the relay opened key 5 and broke the electrolyzing current and the next moment the closing of key 6 put the voltmeter across the poles of the cell.

4. *Errors of the Observations.* — When the voltmeter was thus placed across the terminals of the electrolytic rectifier, after the electrolyzing current had been broken, the indicator of the voltmeter would quickly swing up to a position depending on the applied electromotive force and the temperature of the cell, and would fall back more slowly to a comparatively small value.

It will be evident that the method was not one of great precision, there being at least two errors which could not be accurately determined. First the momentum of the moving system of the voltmeter would tend to carry the pointer beyond the true reading, by an amount depending upon the voltage to be measured. It was found by repeated observation, by quickly applying a constant voltage for a short time to the voltmeter that if the voltage applied was 14 volts, the pointer would swing to a position indicating 15 volts and that if the applied voltage was 30 volts the pointer would be carried to a position indicating 32 volts, showing that the momentum of the system caused an error of about six and two thirds per cent. This, however, depended on the time during which the electromotive force was applied. The percentage here given is that for infinite time. Secondly there exists an error due to the decrease of the counter electromotive force, during the interval between breaking the electrolyzing current and making the voltmeter circuit. This interval was short, but as the polarization diminished very rapidly at first, the error may have been several per cent. We may also include in this error the error due to the time required for the pointer of the voltmeter to swing up to its maximum reading. The value of this second error could not be determined with the apparatus used, and no correction has been made for it. The data in the tables are corrected for the error due to momentum. It will be observed that the second error, not corrected for, decreases the true value of the counter E.M.F.; accordingly the values recorded are not so great as the true values.

5. *Measurements of the Counter E.M.F.* — In the following tables are given a series of sets of measurements of the counter electromotive force of the electrolytic rectifier, at various temperatures and conditions of the cell. Four represesentative sets at temperatures 1°, 23°, 48° and 58°, respectively with aluminum as anode and one at 1° with aluminum as kathode are recorded. These determinations were several times repeated with results agreeing substantially with those recorded.

Measurements of applied E.M.F. current and counter E.M.F. at 1° with a well-formed aluminum anode and a carbon kathode are given in Table I.

TABLE I.

Temperature 1°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
2.1	.0002	1.9	28.0	.0040	24.5
4.5	.0003	3.3	30.0	.0045	26.2
6.7	.0005	6.0	32.0	.0075	26.8
9.0	.0007	7.6	34.0	.0160 ?	27.6
11.2	.0010	9.8	36.4	.0165	28.8
13.5	.0015	11.6	38.7	.0220	30.0
15.5	.0020	13.5	41.0	.0250	31.0
17.4	.0025	15.0	43.2	.0275	31.2
19.5	.0025	17.0	45.0	.0460	31.0
21.3	.0027	18.8	47.2	.1100	29.0
23.4	.0031	20.7	49.3	.1800	27.0
25.7	.0036	22.6	51.0	.5000	19.0

The data from this table are exhibited in the curve in Fig. 2 so far as 30 volts. Curve *I* exhibits the applied E.M.F. and current. Curve *II* exhibits the counter E.M.F. and current. Curve *III* exhibits the electromotive force from Ohm's law, assuming the resistance to be constant at 2 ohms, the value obtained from a series on measurements by Kohlrausch's method.

Table II. gives the data for the same cell under the same conditions with aluminum as the kathode.

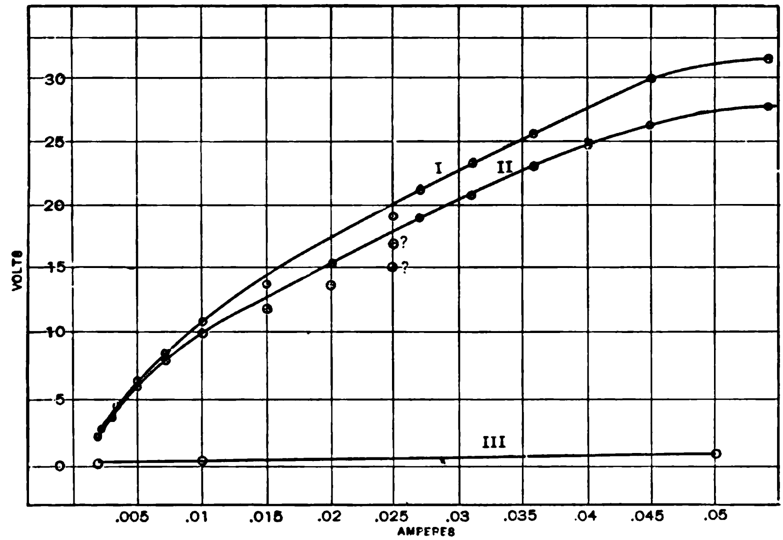

Fig. 2. Applied Counter and Reversed E.M.F.

TABLE II.

Temperature 1°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
1.07	.020	0.4	1.5	.150	0.8
1.2	.020	0.4	2.0	.300	1.25
1.3	.050	0.6	2.5	.500	1.5

Tables III., IV. and V. give applied and counter E.M.F. of the same cell for temperatures 23°, 48° and 58° respectively.

TABLE III.

Temperature 23°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
2.0	.0002	1.2	19.6	.0046	16.0
4.4	.0009	3.0	21.0	.0060	17.0
6.4	.0012	5.0	23.0	.0110	19.0
8.5	.0015	7.0	25.2	.0160	20.0
10.2	.0019	9.0	27.0	.0320	21.0
13.0	.0022	11.0	29.0	.0900	21.0
15.2	.0025	12.0	32.0	.2250	21.0
16.7	.0035	14.0	32.2	1.2000	19.0

TABLE IV.

Temperature 48°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
2.1	.0002	1.2	20.0	.0120	17.0
4.4	.0020	3.0	22.2	.0700	16.0
6.8	.0030	4.5	24.3	.1600	16.0
9.0	.0040	7.0	26.2	.2100	16.5
11.3	.0050	9.0	28.5	.2250	18.0
13.8	.0065	10.5	31.0	.2500	19.0
16.0	.0080	12.5	33.0	.3100	19.8
18.2	.0115	15.5	34.7	.6000	19.0

TABLE V.

Temperature 58°.

Applied E.M.F.	Amperes.	Counter E.M.F.	Applied E.M.F.	Amperes.	Counter E.M.F.
2.0	.075	0.5	19.4	.280	11.3
4.2	.120	2.0	21.2	.340	13.0
6.4	.140	3.8	23.2	.425	14.0
8.5	.160	5.0	26.2	.460	15.0
11.0	.185	6.5	28.2	.550	16.5
13.0	.200	8.0	29.8	.860	17.0
15.0	.250	9.0	31.0	1.300	16.0
17.5	.250	10.0			

The data from the respective Tables I., II., III. and V. are exhibited in Fig. 3.

Curves *I* and *I′* exhibit the relation of the applied and counter electromotive forces to the current, the temperature of the cell being 1°.

Curves *II* and *II′*, and *III* and *III′* exhibit similar data from Tables III. and V. respectively at temperature 23° and 58°, and curve *IV* exhibits the data from Table II. giving the applied E.M.F., when the aluminum is the kathode, at a temperature of 1°.

The effect of temperature upon the apparent resistance of the aluminum anode is very marked. At temperatures not much above 55° the very rapid increase in current at a certain critical electromotive force is hardly perceptible, while at temperature below 50° the position of the critical value of the electromotive force is clearly defined. The value of the critical electromotive force decreasing as the temperature increases at the rate approximately of 1 volt per degree between 1° and 23°.

6. *Discussion of Data.*—A comparison of the applied and counter electromotive forces in Tables I., III., IV. and V. and their corresponding curves, Figs. 2 and 3, show that eighty-five to ninety-five per cent. of the apparent resistance is accounted for by the counter electromotive force and it only remains to explain the cause of this very high counter electromotive force and account for the breaking down of the high apparent resistance at a comparatively high electrical pressure. So long as the applied electromotive force remains below a certain critical value depending on temperature, a uniform whitish film of an oxygen compound of aluminum is formed over the surface of the aluminum anode. This film can be shown to be extremely hard, compact, non-crystalline and apparently insoluble in the electrolyte. The ohmic resistance of the film has also been shown to be very high.

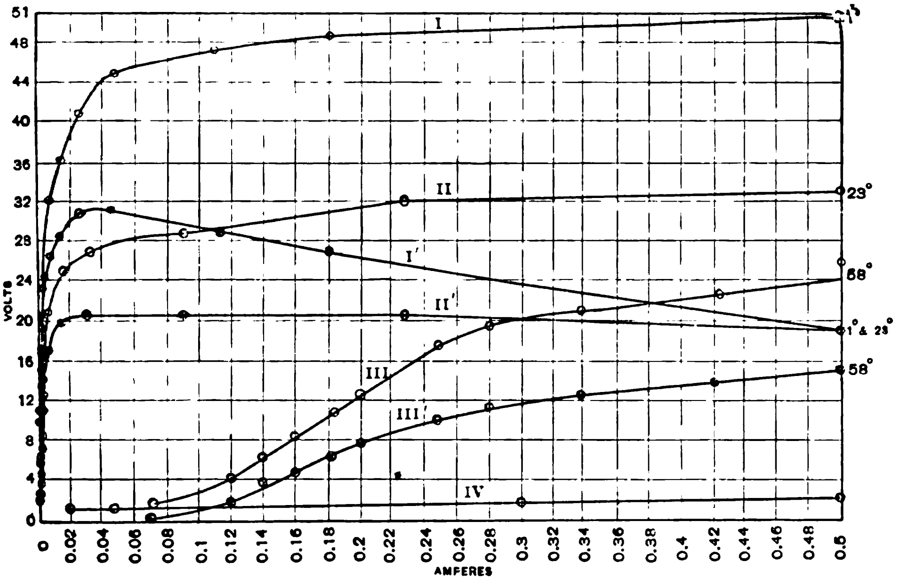

Fig. 3. Applied and Counter E.M.F. for Different Temperatures.

When, however, the applied electrical pressure is greater than a certain critical value this film of alumina changes from a white non-crystalline substance to a dark crystalline substance. These dark crystalline formations occur in parts of the plate only and they always begin to form at those parts where the oxygen is found in the greatest quantities. This dark crystalline formation has very much the appearance of corrundum or emery. If a plate is removed at this stage and carefully examined it will be found that the dark parts are elevated and rough to the touch. When examined with a microscope, of forty diameters magnifying power, the crystalline formation can be easily seen and frequently not only dark corundum-like crystals but crystals of brilliant colors could be easily detected. On a very superficial examination, these brilliantly colored crystals have the appearance of being small crystals of ruby and sapphire.

The formation of crystals exposes the metallic surface of the aluminum plate to the action of the electrolyte and allows the anions to discharge to the anode increasing very rapidly the current, while the continued formation of the crystals, so long as the electrical pressure is greater than the critical value, continues to expose fresh surfaces of the metallic aluminum to the action of the anions. When the critical value of the applied electromotive force has been reached it will be observed that the counter electromotive force decreases and the current greatly increases as the applied electromotive force is increased. That is, as soon as the anions can give up their charge to the metallic aluminum the counter electromotive force decreases. The very high counter electromotive force then is due to the presence of a large number of charged ions around the aluminum plate. These anions (possibly SO_4) are prevented from reaching the metallic conductor by the whitish film of alumina that has been formed on the anode. A further evidence of the presence of this wall of charged ions is given, if a conductor is brought near the anode, when there is a high counter electromotive force, a spark discharge will occur in the solution between the conductor and the layer of charged ions and at the time of the discharge the current greatly increases. It is not believed that this momentary increase of current is due to any rupture of the film but simply to the renewing of the layer of anions which had lost their ionic condition by discharging to the conductor.

Still another experiment shows the existence of this layer of charged ions. The electrolytic cell was under an electrical pressure of 26 volts with a counter electromotive force of 17.5 volts, giving .07 ampere of current. Air bubbles were forced into the solution and caused to pass over the surface of the aluminum anode. The current rapidly increased to 0.35 ampere and fell again to .07 ampere, when the bubbles ceased. The pointer of the milliammeter responded very quickly to the passage of a large bubble over the surface of the anode but it was not possible to measure the decrease of the counter electromotive force under these conditions. The temporary increase of the current may be explained by the temporary destruction, in part, of the concentration series, by the passage of the air bubbles over the plates.

If the electrical pressure is maintained for some time above the critical pressure the film of alumina not only forms crystals but is dissolved by the solution, forming depressions in the plate where the crystallization had produced elevation. This dissolving of the dark crystalline formation was observed by Norden and was made the basis of his theory of the aluminum anode. I think, however, that it is very doubtful that the white alumina is dissolved by the solution even by long standing. The crystalline formation may however either be dissolved by the solution or it may separate from the plate and fall into the solution in the granular form. By maintaining the voltage above its critical value for several hours an aluminum anode that had been formed with the dark crystalline formation, was largely dissolved by the electrolyte. This dissolution of the crystalline formation does not however offer an explanation of the anodic phenomenon.

The explanation given by Burgess and Hambuechen is also based upon the idea of a non-conducting film which changes its properties rapidly when the current is reversed. As already stated when the aluminum is the anode oxygen is the secondary product of the discharge anion. The oxygen unites with the aluminum, forming a film over the surface of the anode. When aluminum is the kathode hydrogen is the secondary product of the kation and is set free. The kation also discharges to the metallic surface of the aluminum. If the film is already formed hydrogen gas is formed between the metallic surface and the film, breaking away small areas of the film. It was probably these small areas that Burgess and Hambuechen considered the valves through which the current passed and into which they deposited copper.

When aluminum is the anode and the potential is less than the critical value, it has been shown that there is formed a film of alumina on the surface of the aluminum, which prevents the anions from discharging to the metallic surface of the anode, thus causing the formation of a layer of charged ions around the plates which produces a high counter electromotive force. This high counter electromotive force decreases the effective potential and manifests itself as a high apparent resistance.

7. *Determination of the Rate of Increase of the anions Around the Anode.*— In accordance with the theory that the ions would discharge their electricity when the free metallic surface was exposed by the crystallization of the aluminum; it became important to know whether a free metallic aluminum surface would conduct an electrical current as freely when it was the anode as when it was the kathode. In order to determine the conductivity of a free metallic surface of aluminum, a plate was freed from all oxide film by scraping with a sharp tool after the application of turpentine, thus giving a very bright metallic surface. The plate was then made the anode of an electrolytic rectifier with carbon as kathode and the data in the following table were obtained, the applied E.M.F. being constant at 26 volts.

Table IV.

Time			Amperes.	Counter E.M.F.	Time			Amperes.	Counter E.M.F.
Hr.	Min.	Sec.			Hr.	Min.	Sec.		
1	42	30	9.000	0.2	1	47	00	.130	16.0
1	42	35	1.500	0.5	1	48	00	.135	16.5
1	42	45	.300	3.0	1	50	00	.130	17.0
1	43	45	.250	7.0	1	55	00	.120	17.0
1	44	30	.190	15.0	2	00	00	.105	17.0
1	45	30	.150	15.0	2	10	00	.090	17.5
1	46	30	.145	16.0	2	50	00	.070	17.5

The curves exhibiting the relation between the time and the current, and the time and the counter E.M.F., are given in Fig. 4. Curve *I* shows the very rapid fall of the current from 9 amperes to

.07 ampere. Curve *II* shows the rapid increase of the counter electromotive force, and curve *III* exhibits the constant current when aluminum was the kathode. Although the value of the current as first measured when aluminum was anode is not so great as its constant value when aluminum was the kathode, the very close approximation to the constant kathodic value is a strong argument in favor of the theory that the first anions (SO_4) discharge their electricity when in contact with the metallic aluminum and that it is the formation of the negative ions in a concentration series or the presence of the free oxygen, evolved from the union of SO_4 with H_2O; in process of union with the aluminum that produces the high counter electromotive force which reduces the current to aminimum.

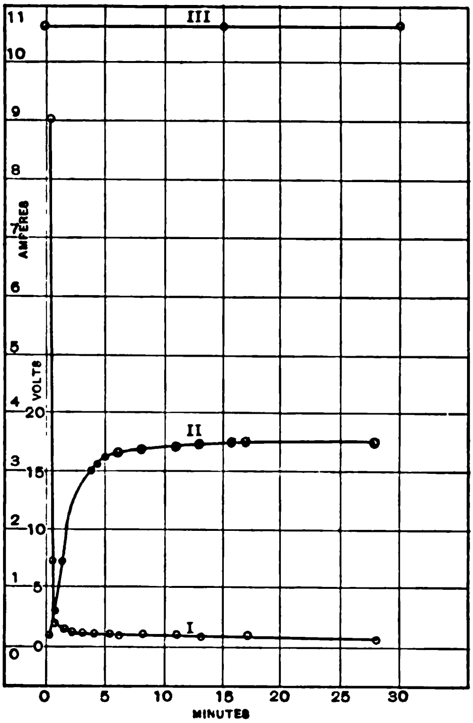

Fig. 4. The rate of Formation of an aluminum Anode and the Development of the Counter E.M.F.

8. *Is the Oxygen Added Directly to the Aluminium?* — An effort was made to answer this question by the following experiments:

A large H cell was constructed. Each leg of the cell was fitted with a carefully weighed aluminum electrode, a thermometer, and a graduated tube for receiving and measuring the gas given off. The cell was filled with a solution of potassium aluminum sulphate, placed in a constant temperature bath and a current passed through until a measured quantity of hydrogen was liberated. The electrodes were then removed, weighed and the gain or loss determined. Four independent experiments were performed and the following observations and notes were made:

First Experiment. — The aluminum electrode exposed a clean metallic surface to the electrolyte. The temperature of the cell was 15°.

Results from first experiment :

Weight of anode before the experiment,	24.3915	grams.
Weight of anode after the experiment,	24.3997	grams.
Gain in weight of anode during experiment,	.0082	grams.
Weight of kathode before the experiment,	23.9955	grams.
Weight of kathode after the experiment,	23.9949	grams.
Loss in weight of kathode,	.0006	grams.
Hydrogen liberated at kathode,	59	c.c.
Oxygen liberated at anode,	0	c.c.
Amount of oxygen that should have been liberated,	.0415	grams.

On the theory that the oxygen is added directly to the anode this experiment should have given an increase in the weight of the anode of .0415 gram, while it gave only .0082 grams of oxygen or about one fifth the amount required. However, this experiment shows that the oxygen does not remain in the gaseous form and must be accounted for either by assuming that it forms a soluble compound with the anode, and is then dissolved by the electrolyte, or that it forms an insoluble compound with the anode, part of the anode being dissolved by the electrolyte to account for the discrepancy. Norden[1] concluded that the electrolyte acts chemically on the anode at ordinary temperature, and in my own work I have been successful in dissolving a large part of an aluminum anode after it had been formed with the dark formation. In order to account for the loss by dissolution the experiment was repeated with the cell in an ice-bath.

EXPERIMENTS 2 AND 3 WITH THE H CELL.

The H cell arranged as in the former experiment was packed in ice and allowed to reach a temperature of 1°. At first an electromotive force of 33 volts was applied and the amperage during the three hours and twenty minutes fell from 0.105 ampere to .008 ampere. The electrical pressure was then increased to 52 volts and the amperage soon became constant at .07 ampere. In three hours 70 c.c. of hydrogen was liberated at the kathode. No gas was liberated at the anode.

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[1] L. c.

The anode showed a gain during the experiment of .0318 grams and the kathode a loss of .0045 grams. If all the oxygen set free from the electrolyte had been added to the anode, and there had been no dissolution of the anode during the experiment there should have been an increase of .0501 grams, showing a discrepancy of .0184 grams; that is, about thirty-six per cent.

The experiment was again repeated under the same conditions and the anode showed, for 55 c.c. of hydrogen liberated, a gain of .0243 instead of .0372 grams, a discrepancy of .0149 or forty per cent.

It was here observed that some of the oxygen collected at the upper end of the anode and that most of the formation was at this place. It was also observed that the dark formation showed signs of having been dissolved by the electrolyte. To prevent this dissolution of the formed anode a band of india rubber was fitted over that portion of the anode which passed through the surface of the solution, and the experiment was again repeated at a temperature of 0°.

For the fourth experiment the following results were noted: 25 c.c. of hydrogen was liberated. The increase in weight of the anode was .0237 gram. The weight required to account for 25 c.c. of hydrogen is .01792 gram, the excess of weight at the anode being .00583 gram.

Although these experiments have by no means been conclusive in showing that the oxygen is added directly to the aluminum as Al_2O_3, they nevertheless show that the oxygen does not remain as a gaseous film around the anode, producing an ohmic resistance, and they also show that the oxygen is added to the aluminum as a chemical compound; either, with Norden, as the normal aluminum hydroxide, $Al_2(OH)_6$, or as I believe more probable as aluminum oxide, Al_2O_3, with water of crystallization in that part of the oxide which crystallizes. It is also possible, according to Norden's analysis, that some of the sulphate is added to the solid formation of the aluminum anode. The problem of the exact composition of the formation on the aluminum anode at the different stages of its formation is one of great interest and I believe will merit the most careful investigation.

SUMMARY OF RESULTS AND CONCLUSIONS.

1. I believe the foregoing experiments have been conclusive in showing that the apparent resistance of the aluminum anode in potassium aluminum sulphate is not an ohmic resistance but a resistance of transition of the ions, primary or secondary, and that this resistance of transition manifests itself in a counter electromotive force. The formation of the film of alumina which is a very poor conductor of electricity on the surface of the aluminum anode prevents the anions from reaching a conducting surface and thus discharging. The anions, therefore, become massed around the positive plate in a layer of highly charged radicals ($\dot{S}O_4$) or in a layer of highly charged atoms of oxygen which are in the act of entering into union with the metallic aluminum.

2. When the aluminum is the kathode hydrogen is the primary or secondary product at the aluminum surface and there is no chemical union at either the aluminum or carbon surfaces, if the aluminum surface is already covered with a film of alumina. The kation finds access to the metallic surface of the aluminum plate and hydrogen is set free between the film of alumina and the metallic aluminum, thus separating the two surfaces and exposing the metallic aluminum to further action of the kations.

3. It has been shown that when the electrical pressure is greater than its critical value the film becomes crystalline in structure and in crystallizing exposes free metallic surfaces to the action of the anions, allowing them to discharge to the metallic surface.

4. The value of the critical pressure and also the counter electromotive force depends upon the temperature. The critical electromotive force for 1° is approximately 47 volts and for 48° only 22 volts; the counter electromotive force increasing with decrease of temperature.

5. On account of the very high resistance of the film of alumina formed over the aluminum anode the anions do not give up their charge to this film, but must pass through to the metallic aluminum. When the anions have discharged the oxygen set free by secondary action of the radical SO_4 unites with the aluminum, thus increasing the film and decreasing the possibility of other anions reaching the metallic aluminum.

6. It has been shown that the high anodic resistance depends upon the temperature, and that at temperatures approaching the temperature at which aluminum decomposes water, *i. e.*, 100°, the high anodic resistance greatly decreases, thus showing that the anodic resistance depends upon the chemical conditions for the union of aluminum and oxygen.

7. The theory as here presented accounts for the following observed conditions and phenomena relative to the electrolytic rectifier. First, it explains the apparent high resistance of the aluminum anode and low resistance of the aluminum kathode. Second, it explains the critical electromotive force and the good conductivity of the anode above this critical pressure. Third, it explains the very great change of conductivity with change of temperature. Fourth, the increased weight of the anode is a direct result of the theory. Fifth, the good conductivity of the electrolyte when the aluminum has a metallic surface also follows from the theory.

In conclusion, it may be said that sufficient data have been obtained to explain many of the phenomena of the electrolytic rectifier; there are however still some interesting phenomena not explained; as, the exact composition of the film on the aluminum anode, the cause of the crystallization at and above the critical potential, the dissolution of the crystalline formation by the electrolyte, and the exact ionic condition that produces the high counter electromotive force. It is believed however that these problems are not beyond the possibility of being determined by careful investigation and it is the intention of the writer to investigate these conditions as soon as possible.

Physical Laboratory, Case School of Applied Science,
Cleveland, Ohio, July 22, 1903.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS IN METHYL ALCOHOL IN THE NEIGHBORHOOD OF THEIR CRITICAL POINT. I.[1]

BY CHARLES A. KRAUS.

THE electrical conductivity of solutions has recently been applied to the study of the critical phenomenon.[2] It has been shown, not only, that solutions conduct beyond the critical point, but that the vapors of these solutions become conducting[3] before the critical point is reached. In the immediate vicinity of the critical point the temperature coefficient of the solution undergoes a change, resulting in a diminution of the coefficient. The dielectric constant, too, has been studied by Eversheim,[4] and follows in a general way the electrical conductivity of the solution.

The present paper treats mainly of two points in connection with the conductivity of solutions in the critical region; the change of the conductivity in the immediate neighborhood of the critical point, and the change of the conductivity with varying density of solvent fluid beyond the critical point.

One of the difficulties encountered in the work dealing with the conductivity at the critical point, has been the high value attained by the resistance. Hagenback[4] points out that the resistance of a solution in liquid sulphur dioxide increases a thousand times, in round numbers, in heating up to the critical point from ordinary temperatures. This circumstance leads to the use of complicated measuring apparatus and concentrated solutions, both of which are disadvantageous.

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[1] The discussion of results is given in the concluding portion of this paper which is to appear in the following number of the REVIEW.—Ed.

[2] Franklin and Kraus, Amer. Chem. Jour., 24, p. 83, 1900. A. Hagenback, Phys. Zs., 1, p. 481, 1900; Ann. der Phys., 5, p. 276, 1901, and 8, p. 539, 1902. P. Eversheim, Ann. der Phys., 8, p. 539, 1902; Phys. Zs., June 15, 1903.

[3] A. Hagenback, l. c., Ann. der Phys., 5, p. 286.

[4] P. Eversheim, l. c.

[5] A. Hagenback, l. c., 5, p. 301.

Some years ago Franklin and Kraus[1] showed that for a large number of solutions in liquid ammonia the maxima of electrical conductivity lay within a comparatively narrow range of temperature about 100° below the critical point. Walden and Centnerszwer[2] have shown similar relations to hold true for solutions in sulphur dioxide. The same has long been known to hold true for certain water solutions. The regularity of the curves leads one to suspect that if one were able to find a solvent in which the conductivity maximum lay sufficiently near the critical point, the conductivity beyond the critical point would be considerable.

Now water solutions must possess maxima of conductivity that lie very near their critical point, if not beyond it.[3] The solvent power for glass makes the use of water as a solvent difficult in this instance. This has led the author to study the maxima of conductivity of the alcohols, compounds possessing many properties in common with water.

A solution of potassium iodide in ethyl alcohol reached its maximum of conductivity in the neighborhood of 100° C. It remained a conductor beyond the critical point, but the resistance attained considerable magnitude. In the immediate neighborhood of the critical point a considerable quantity of solute crystallized out on the walls of the tube, going into solution again as the temperature was somewhat increased.[4]

Solutions in methyl alcohol proved more promising. For a solution of potassium iodide, the maximum was found in the neighborhood of 160°. The conductivity beyond the critical point was found to be remarkably high. As will appear from the results given below, the conductivity just beyond the critical point has fallen to one tenth its maximum value, which is only a trifle less than one half its value at ordinary temperatures. Adding to its high conductivity, the ease of preparing and manipulating its solutions, methyl alcohol seems an ideal substance for the subject in hand. It possesses, however, some drawbacks, which, while not sufficient to affect materially the results aimed at in this paper, are yet of such a nature as to make exact measurements and comparisons difficult. Its high critical temperature makes it somewhat difficult to supply a constant temperature bath. The greatest drawback, however, is the tendency of alcohol to enter into reaction with any substance dissolved in it. Of a large number of substances dissolved in methyl alcohol, only the alcoholates and the bases were found to suffer a comparatively small change in conductivity on heating up. It was found, however, that the reaction was not as serious a matter as was anticipated. The reaction went on at a rapid rate and apparently went on to completion, for after once heating up, the conductivity remained constant thereafter. It appears that Hagenback[1] experienced some difficulty of this kind in sulphur dioxide. In some cases it was found that the critical point of alcohol solution was changed (lowered) on repeated heating. There also appeared to be some gas occluded on the electrodes. The tendency would naturally be for this gas to lower the critical temperature. With respect to the temperature measured from the critical point however, the conductivity remained constant, so that comparisons may still be made with regard to the critical point. This is probably the proper method of comparison any way, for a change in concentration of the solution will shift the critical point. The manner then in which this particular circumstance has affected the results is in giving to the temperatures a relative rather than an absolute value.

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[1] Franklin and Kraus, l. c.

[2] Walden and Centnerszwer, Zs. f. Phys. Chem., 39, p. 514, 1901–2.

[3] A. Hagenback, l. c., 5, 305; Arrhenius, Zs. f. Phys. Chem., 4, p. 96, 1889.

[4] This phenomenon may be of the nature of that investigated by Smits. Zs. f. Elec. Chem., no. 33, p. 663, Aug. 31, 1903.

The nature of the reaction in the case of potassium iodide is doubtful. The odor obtained on opening the tube was suggestive of methyl iodide. The potassium would probably be present then as hydroxide or alcoholate. The maxima obtained in the case of alcoholate and hydroxide did not agree with those of the potassium iodide solution. The nature of the change must be left open for the present. Before exact results can be obtained at the critical point we must know the nature of the reactions occurring. It is hoped to take up this point subsequently, in a more extended study of the maxima of the alcohol solutions.

The measurements were carried out in a tube of approximately 1.5 mm. internal diameter and 2 mm. wall. The tubes had a length of from 12 to 20 cm. The electrodes were from 1.5 to 2 cm. long and 1 mm. wide. They were held in relative position by small bits of glass. The connections through the glass tube were made with platinum of 0.04 cm. diameter. This size of wire is still sufficiently large to allow of ready manipulation, while it is so small that the glass is not appreciably weakened by its presence. To prepare a tube a piece of tubing of the dimensions given was selected. At one end this tube was drawn down so as to form a shoulder (*A*, Fig. 1). About 0.5 cm. beyond this shoulder the tube was drawn off. A small thick bulb (*B*) was blown on this end of the tube, and by means of a bit of glass two fine capillaries (*DD*) were drawn on this bulb. After cutting off the capillaries near the bulb, the electrodes (*C*) were introduced, the wires projecting each through one of the capillary tubes. The tube was now heated in the blow-pipe flame, taking care to heat the glass rather than the platinum wires. The bulb thickened and assumed a tubular form of considerable uniformity. The object of this operation was to seal the electrodes into the tube with a minimum thickening of the glass, *i. e.*, the whole tube, end and wall, were to be of as uniform dimensions as possible. While the tube was still in the flame the end was drawn out by pulling gently on the platinum wires until the electrodes rested on the shoulder (*A*) at the bottom of the tube. The tubes prepared in this way seemed to possess all the strength of the original glass tube. With tubes of the dimensions specified not a single explosion resulted. The tubes were tested by heating up twenty degrees or more, beyond the critical point.

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[1] A. Hagenback, l. c., 5, p. 295.

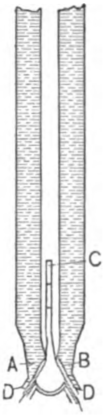

Fig. 1.

The tube was plantinized and the resistance of the leads and the resistance capacity of the cell were determined. The open end of the tube was then drawn down into a long thick-walled tube of about 0.5 mm. internal diameter, and to make the total length of the tube shorter this tube was bent at an angle 60° to the rest of the tube. The volume of the tube and the volume per unit length were determined. The tube was finally washed with pure solvent and dried. After introducing the solution the tube was placed in a bath of liquid ammonia, and the pressure was reduced as far as the vapor pressure of the alcohol would allow, when the tube was sealed. Before attaching the tube to the pump the capillary was drawn out very fine at one point in order to facilitate sealing off.

The heating was carried out in melted paraffine. The bath was constructed of a large beaker placed in a brass jacket with asbestos packing between. Glass-covered windows were left opposite each other for the purpose of observation. The heating was done electrically with a lamp-board resistance for control. This has many advantages over a flame for heating purposes. By means of hand regulation it was easy to keep a thermometer adjusted to a few hundredths of a degree. The heating coils were mounted on a glass frame and were distributed around the stirrer which was run by a small motor. The proper distribution of the coils around the stirrer added much to the constancy of the heating arrangement. While the temperature could be kept adjusted to 0.02° at any point in the bath, there was some variation in the different levels of the bath. For the space occupied by the tube, the variation did not exceed 0.05°, while the results justify the conclusion that for the electrode space the variation was considerably less than this. In the arrangement used the top of the bath was open to the air and a portion of the paraffine vaporized. This caused a cooling off of the bath and the top of the bath was the cooler. If this circumstance could be removed, this bath would give much better results than were possible with the arrangement used. For work that does not require the limit of accuracy the form of bath used can be recommended both for convenience and constancy. Perhaps it would not be amiss to add a few words in regard to the details of the preparation of the bath. A semicircular framework was made up of glass rods. On this framework the coils were stretched not only around the sides but also over the top and bottom. Two glass rods with their ends bent into closed rings of about .5 cm. diameter were sealed, one to the bottom of the frame, the other on longer supports attached to the top of the frame, and projecting over the beaker. A glass rod was chosen to fit the glass bearings and as many vanes were mounted on this rod as were desirable. The vanes were thus surrounded on all sides by coils except toward the diameter of the semicircle. The tube was placed in this remaining semicircular space.

In order to read the volume of the liquid in the tube a milk glass scale was placed back of the tube and attached to it. The tube and scale were suspended in a carriage which could be put into, or taken out of, the bath without disturbing the rest of the apparatus. When accurate readings of volume were required the paraffiine bath had to be changed every other series. A weight and wire attached to one end of the scale and tube enabled the operator to invert the tube at will. The whole apparatus was placed under a hood and the tube was observed by looking through the window.

The conductivity was measured by means of a Kohlrausch bridge and telephone. The minimum was excellent except in the case of the highest resistances which were reached in only one series of measurements. But even in this case it was possible to set within a couple of millimeters. For measuring the temperatures two thermometers were used, one divided into tenths, the other divided into degrees. The one divided into tenths was used near the critical point. The temperatures were finally corrected by comparing them with a standard which was completely immersed while those to be calibrated were immersed as they were in the measurements. The conductivity of the glass comes into question in a measurement of the conductivity at high temperatures. The tubes empty did not indicate with the bridge a conductivity which could affect the results by more than a few per cent. with the highest resistances. With the smaller resistances the conductivity of the glass could not affect the results. The relative area of the conducting surface of glass to that of solution was about 1 to 20, so that with the solution twice as good a conductor as the glass the error would be a trifle over 2 per cent.

To change the quantity of solvent, keeping the quantity of solute constant, the tube was connected with a vessel containing sulphuric acid. The whole apparatus was then exhausted as far as the vapor pressure of the alcohol would allow. A small wire carrying a current was passed around the outside of the tube near the surface of the liquid. This heated the surface of the liquid and produced evaporation without danger of losing a portion of the solute. Liquid could be introduced by cooling the tube in a bath of liquid ammonia, connecting with a reservoir of alcohol, and exhausting. It was found preferable, however, to change the quantity of solvent by evaporation.

Constants and Units.

The resistance capacity of the tube was determined by means of a 0.1 *n*-solution of potassium chloride.[1] In the following tables the constant is given under K. Under $S \times 10^6$ are given the uncorrected values of the specific conductivity referred to Kohlrausch units[2]; the values actually appearing in the table are the products of the specific conductivities with 10^6.

V_t / V gives the ratio of the volume of the liquid at the temperature t to the total volume of the tube. Because of the unknown nature of the reaction taking place in the solution, the conductivities are not expressed in molecular values. The conductivities corrected for change in volume appear under $S \cdot V_t / V \times 10^6$. This is simply the product of the specific conductivity by the ratio of the volume of the liquid at temperature[3] t to the volume beyond the critical point. This method of correction has been adopted in preference to any other because in this case the actual specific conductivities appear above the critical point. The corrected value of the conductivity appears in all the curves.

To obtain the molecular conductivities the corrected conductivities need only be multiplied by a constant, which can be determined from the concentrations of solutions given and the volume of the tube.

How the correction affects the inclination of the curves will be discussed later. Under C appears the concentration of the solution in per cent. of solute. Whenever alcohol was extracted from a solution without removing solute, C refers to the concentration before the removal of the solute. The total volume of the tube at 240° is given under V. Under W appears the weight of the solution.

Unless otherwise stated the tubes were heated up to the critical point until no further change took place in the conductivity.

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[1] Kohlrausch, Holborn and Diesselhorst, Wied. Ann., 64, p. 417, 1898; Kohlrausch and Holborn, "Das Leitungsvormögen der Electrolyte," p. 1, 1899.

[2] Kohlrausch and Holborn, l. c.

[3] Compare A. Hagenback, l. c., 5, p. 292.

NUMERICAL RESULTS.

Series I.

Potassium Iodide. Curve 1, Fig. 2.

$K = 0.1321$, $C = 0.01855$ *per cent.*, $W = 0.11169$ *g.*, $V = 0.3715$ *c.c.*

Liquid.			
t	$S \times 10^6$.	V_t/V	$S \cdot V_t/V \times 10^6$.
90.0	908.4	0.4324	392.8
102.0	1,006.0	.4363	438.9
123.0	1,098.0	.4451	488.2
138.2	1,126.0	.4548	511.9
149.0	1,139.0	.4674	532.3
159.0	1,126.0	.4764	536.2
171.0	1,076.0	.4853	522.5
183.8	1,006.0	.4979	500.9
197.0	740.4	.5095	377.3
208.5	617.0	.5137	314.3
220.0	431.2	.5445	234.8
225.0	337.5	.5569	187.9
230.0	252.1	.5693	143.5

SERIES II.

Potassium Iodide. Curve 1, Fig. 2; Curve 9, Fig. 3.

Constants of tube and of solution as in I. In Fig. 3 all curves are referred to the same critical temperature for the sake of convenience and comparison. The temperatures of series I. are those used as scale.

Liquid.			
t	$S \times 10^6$.	V_t/V	$S \cdot V_t/V \times 10^6$.
237.0	186.0	0.6005	111.6
238.0	157.6	.6094	96.05
238.5	143.7	.6183	88.88
239.0	127.0	.6275	79.69
239.5	107.5	.6362	68.39
240.04	83.71	.6628	55.50
240.4	63.92	.7432	47.50
240.5	55.46	.8074	44.78
240.6	45.29	.9566	43.32
Crit.	42.65	1.000	42.65

Gas.			
t	$S \times 10^6$.	t	$S \times 10^6$.
240.7	42.14	242.45	36.10
240.8	41.56	243.4	34.45
240.9	40.98	244.4	32.88
241.0	40.41	245.46	31.24
241.2	39.52	247.1	29.11
241.4	38.68	249.1	26.59
241.6	37.89	252.0	23.92
241.92	37.06		

Series III.

Ammonium Chloride. Curve 2, Fig. 2.

$K = 0.1316$, $C = 0.2245$ *per cent.*, *tube* 1/3 *full at* 20°.

Liquid.			
t	$S \times 10^6$.	V_t/V.	$S \cdot V_t/V \times 10^6$.
71.0	3,556.0	.3833	1,363.0
85.1	3,744.0	.3897	1,460.0
94.6	3,851.0	.3927	1,512.0
105.2	3,948.0	.4006	1,581.0
116.2	4,058.0	.4021	1,631.0
124.7	4,108.0	.4087	1,679.0
135.0	4,159.0	.4147	1,722.0
144.0	4,176.0	.4174	1,743.0
165.4	4,094.0	.4234	1,733.0
174.8	4,042.0	.4261	1,723.0
183.8	3,929.0	.4300	1,690.0
194.0	3,769.0	.4333	1,633.0
204.0	3,528.0	.4359	1,538.0
214.0	3,241.0	.4411	1,430.0
219.0	2,777.0	.4464	1,240.0
224.0	2,533.0	.4461	1,130.0
229.2	2,003.0	.4453	892.1

Series IV.

Ammonium Chloride. Curve 2, Fig. 2; Curve 8, Fig. 6. Constants of tube and solution as in III.

Liquid.			
t	$S \times 10^6$.	V_t/V	$S \cdot V_t/V \times 10^6$.
234.0	1,524.0	.4411	672.0
236.9	1,236.0	.4333	535.8
239.0	930.3	.4261	430.3
240.0	760.0	.4147	315.2
241.0	605.7	.4000	242.3
241.9	469.7	.3707	158.8
242.5	257.7	.2806	72.33

Vapor.		Gas.	
t	$S \times 10^6$.	t	$S \times 10^6$.
236.9	1.574	243.1	67.25
239.0	2.177	245.2	54.36
240.0	3.568	247.1	47.62
241.0	6.381	249.0	41.33
241.9	14.64	254.0	30.19
242.5	38.66		

Series V.

Potassium Iodide. Curve 3, Fig. 2.

The measurements in this series were obtained with a tube that had not been previously heated above room temperatures. They illustrate, therefore, the reaction that takes place between the solute and the solvent.

Constants of tube and quantity of solute as in I. $W = 0.10688$g.

Vapor.			
t	$S \times 10^6$.	t	$S \times 10^6$.
236.6	0.4220	241.4	2.118
239.0	.5521	241.7	3.449
240.1	.7482	241.8	3.785
241.1	1.544	241.9	6.091

Liquid.

t	$S \times 10^6$.	V_t/V.	$S \cdot V_t/V \times 10^6$.
88.00	162.3	.4209	68.29
114.5	262.4	.4344	114.0
135.5	319.6	.4503	143.9
156.0	401.0	.4674	187.4
176.5	488.3	.4809	239.8
194.5	512.2	.4944	253.3
215.5	399.7	.5119	204.6
227.1	321.8	.5303	170.6
232.1	255.2	.5438	138.8
236.6	181.9	.5569	101.0
239.0	131.7	.5657	74.47
240.1	107.0	.5837	62.50
241.1	80.87	.6045	48.87
241.4	67.0	.6226	43.58
241.7	56.99	.6449	36.76
241.8	52.94	.6585	34.85
241.9	45.28	.6772	30.68
242.0	35.02	.8254	28.91

Series VI.

Potassium Iodide. Curve 10, Fig. 3.

The same tube and solution as in V., but after the solution has been heated until reaction is complete.

Liquid.

t	$S \times 10^6$.	V_t/V.	$S \cdot V_t/V \times 10^6$.
237.1	170.2	.5555	94.58
239.1	131.4	.5657	74.35
240.1	106.9	.5749	61.46
241.1	80.34	.6070	48.76
241.6	77.07	.6365	37.54
241.8	50.86	.6770	34.43
241.9	44.46	.6952	30.98
242.0	37.56	.7537	28.31

Gas.

t	$S \times 10^6$.	V_t/V	$S \times 10^6$.
242.1	28.64	244.1	24.29
242.22	28.21	245.1	23.05
242.4	27.43	246.1	22.08
242.6	26.77	247.1	21.26
242.8	26.23	249.1	19.70
243.0	25.81	252.1	17.67
243.5	25.20		

Series VII.

Potassium Iodide. Curve 4, Fig. 2.

$K=0.1461$, $C=0.209$ *per cent.*, $V=0.431$ *c.c.*, $W=0.122$ *g.*

Liquid.			
t	$S\times 10^6$.	V_l/V	$S\cdot V_l/V\times 10^6$.
78.2	1,416.0	.3534	500.2
89.0	1,497.0	.3599	538.9
99.6	1,553.0	.3638	565.0
109.5	1,663.0	.3667	615.1
120.2	1,718.0	.3700	647.1
129.3	1,753.0	.3767	666.2
139.5	1,781.0	.3801	688.9
149.5	1,796.0	.3868	700.4
170.4	1,717.0	.3933	686.0
179.2	1,622.0	.3967	653.6
199.2	1,388.0	.4134	578.2
208.5	1,163.0	.4167	488.7
219.1	923.4	.4201	387.9
224.8	790.0	.4167	329.2
234.0	575.8	.4134	238.0
236.0	480.4	.4034	193.7
238.0	378.5	.3933	148.9
239.0	313.7	.3868	121.4
240.0	239.1	.3599	86.06
241.0	165.9	.3100	51.40

Series VIII.

Potassium Iodide. Curve 4, Fig. 2; Curve 7, Fig. 6.

Constants of tube and solution as in VII.

Vapor.		Gas.	
t	$S\times 10^6$.	t	$S\times 10^6$.
235.0	0.6291	243.1	53.48
237.0	0.9230	245.1	47.42
239.0	1.988	247.0	42.86
240.0	3.561	250.3	37.25
241.0	7.575	255.2	32.15
242.0	18.65		

Series IX.

Potassium Iodide. Curve 5, Fig. 6.

The tube was filled one third full of solution. Owing to its concentration, the solution did not pass through the critical point, but collected in the bottom, becoming very concentrated. At 259° there was only a trace of liquid left.

$K = 0.1461$, $C = 2.53$ *per cent.*

Vapor.			
t	$S \times 10^6$.	t	$S \times 10^6$.
234.0	1.500	251.0	49.30
237.2	1.899	253.0	69.26
239.6	2.432	255.0	82.31
243.1	6.135	257.0	104.2
245.0	11.01	259.0	125.3
247.0	16.84		

Series X.

Potassium Iodide. Curve 6, Fig. 6.

Same tube as in IX. with one half the solution removed. In this case the liquid disappeared by evaporating from the bottom of the tube.

Gas.			
t	$S \times 10^6$.	t	$S \times 10^6$.
249.0	1.188	257.0	2.247
251.0	1.360	259.5	5.979
254.0	1.718	262.2	15.49

Series XI.

Potassium Iodide. Curve 11, Fig. 3.

Constants of tube and quantity of solute as in I. $W = 0.09881$ g.

Liquid.			
t	$S \times 10^6$.	V_l/V.	$S \cdot V_l/V \times 10^6$.
238.2	148.6	.4639	68.95
239.2	123.5	.4677	57.79
240.2	91.41	.4685	42.83
240.7	69.04	.4693	32.40
240.9	60.49	.4624	27.97
241.0	55.27	.4535	25.07
241.1	48.39	.4444	21.50
241.2	39.29	.4064	15.97

Gas.

t	$S \times 10^6$.	t	$S \times 10^6$.
241.3	22.79	244.2	17.70
241.4	21.99	245.2	16.81
241.5	21.33	246.2	16.02
241.6	20.78	247.2	15.26
241.7	20.53	248.2	14.59
241.9	20.20	250.2	13.39
242.4	19.72	253.2	12.28
243.2	18.80		

Series XII.

Potassium Iodide. Curve 12, Fig. 3.

Constants of tube and quantity of solute as in I. $W = 0.09125$g.

Liquid.

t	$S \times 10^6$.	V/V.	$S \cdot V_l/V \times 10^6$.
239.9	153.1	.3905	59.80
240.9	116.9	.3905	45.66
241.4	92.76	.3905	36.23
241.6	84.94	.3811	32.41
241.8	75.01	.3725	27.95
241.9	70.77	.3547	25.09
242.0	60.98	.3367	20.53
242.1	48.01	.2898	13.92

Gas.

t	$S \times 10^6$.	t	$S \times 10^6$.
242.2	18.13	243.8	14.24
242.3	16.54	244.8	13.24
242.4	16.04	245.8	12.69
242.5	15.89	246.8	12.07
242.7	15.57	248.8	10.90
242.9	15.32	251.8	9.431
243.4	14.78		

Series XIII.

Potassium Iodide. Curve 13, Fig. 3.

Constants of tube and quantity of solute as in I. $W = 0.07142$g.

Liquid.			
t	$S \times 10^6$.	V_l/V	$S \cdot V_l/V \times 10^6$.
237.1	245.9	.2845	69.93
238.1	219.4	.2734	59.96
239.1	188.8	.2453	46.38
239.6	177.7	.2328	41.22
240.1	159.3	.2148	34.22
240.3	149.8	.2013	30.16
240.4	144.5	.1832	26.49

Vapor.		Gas.	
t	$S \times 10^6$.	t	$S \times 10^6$.
237.1	0.5795	241.7	6.785
238.1	0.7204	241.8	6.639
239.1	1.025	242.0	6.447
239.5	1.217	242.5	6.243
240.1	1.666	243.0	6.023
240.3	2.096	244.12	5.601
240.7	2.909	245.1	5.295
241.0	4.003	246.1	5.001
241.22	5.147	247.1	4.648
241.4	6.216	249.1	4.078
241.5	6.845	252.1	3.487
241.65	6.993		

Series XIV.

Potassium Iodide. Curve 14, Fig. 3.

A tube, constricted to a small capillary at the middle, was filled with solution so that at the critical point the tube was three fourths full of liquid. The tube was heated through the critical point without stirring. In the curve plotted no correction was made for change in volume of the liquid.

$K = 0.1393$, $C = 0.1188$ *per cent.*, $V = 0.464$ *c.c.*, $W = 0.1363$*g.*

t	$S \times 10^6$.	t	$S \times 10^6$.
238.0	422.5	241.5	169.0
238.9	367.0	241.6	152.7
239.9	299.2	241.8	142.8
240.6	253.1	242.0	136.7
241.0	218.4	242.2	132.3
241.2	197.6	242.6	122.1
241.3	183.9	243.1	112.1
241.4	178.0	243.6	108.2

Series XV.

Potassium Iodide. Curve 15, Fig. 4.

Series XV.–XX. were carried out with the same tube containing the same quantity of solute, and quantities of solvent as indicated.

$K = 0.2781$, $C = 0.1188$ *per cent.*, $V = 0.3981$*c.c.*, $W = 0.11636$*g.*

Gas.			
t	$S \times 10^6$.	*t*	$S \times 10^6$.
241.5	56.41	245.0	45.51
242.0	53.95	247.0	41.68
243.0	50.54	250.1	36.97
244.0	47.90		

Series XVI.

Potassium Iodide. Curve 16, Fig. 4.

Constants of tube and quantity of solute as in XV. $W = 0.1023$g.

Gas.			
t	$S \times 10^6$.	*t*	$S \times 10^6$.
241.32	42.24	245.0	28.80
242.0	36.35	247.0	25.79
243.0	32.48	250.0	22.04
244.0	30.59		

Series XVII.

Potassium Iodide. Curve 17, Fig. 4.

Constants of tube and quantity of solute as in XV. $W = 0.09684$g.

Gas.			
t	$S \times 10^6$.	*t*	$S \times 10^6$.
241.6	28.80	245.0	21.25
242.0	26.54	247.0	19.14
243.0	24.23	250.0	16.90
244.0	22.47		

Series XVIII.

Potassium Iodide. Curve 18, Fig. 4.

Constants of tube and quantity of solute as in XV. $W = 0.0815$g.

Gas.			
t	$S \times 10^6$	t	$S \times 10^6$.
241.7	16.56	245.0	7.886
242.0	10.09	247.0	7.081
243.0	9.396	250.0	6.003
244.0	8.626		

Series XIX.

Potassium Iodide. Fig. 4, Plate IV.

Constants of tube and quantity of solute as in XV. $W = 0.0758$g.

Gas.			
t	$S \times 10^6$.	t	$S \times 10^6$.
241.3	4.783	245.0	3.656
242.0	4.468	247.0	3.247
243.0	4.141	250.0	2.824
244.0	3.884		

Series XX.

Potassium Iodide. Curve 20, Fig. 4.

Constants of tube and quantity of solute as in XV. $W = 0.0588$g.

Gas.			
t	$S \times 10^6$.	t	$S \times 10^6$.
239.0	1.892	244.9	1.521
241.0	1.736	247.2	1.387
242.9	1.662	250.1	1.230

Series XXI.

From curves 15–20 the values of the specific conductivity were obtained for the temperatures 245° and 250°. These values are given below and are plotted with the quantities of solvent in curves 21 and 22, Fig. 5.

Solvent.	Density.	$S \times 10^6$	
		245°.	250°.
.1163 g.	.251	45.6	37.2
.1023	.220	28.8	22.0
.09684	.208	21.2	16.83
.0815	.178	8.0	6.0
.0758	.163	3.7	2.8
.0588	.127	1.44	1.2

(*To be Concluded.*)

A CONVENIENT METHOD OF MOUNTING CARBON RESISTANCES.

By Arthur W. Gray.

LONGDEN (Phys. Rev., Dec., 1902, p. 355) has shown how to make a fairly satisfactory high resistance by depositing soot on a plate of glass whose ends had previously been silvered with a wedge-shaped film. A modification of this, which can be very conveniently mounted, is illustrated in the accompanying figure.

A tube of glass is substituted for the plate. The ends after being silvered are snugly wrapped with a ribbon of stout tin foil, which is firmly bound on with copper wire so as to make good contact with the silver. Then the soot is deposited and hardened as described by Longden. To mount the resistance thus prepared, a J-shaped glass tube *AB* and a shorter U-shaped one *CD* are fastened vertically into a block of paraffin as indicated. The lower portions of these tubes are filled with mercury. The resistance tube is simply slipped over the long arm *B* of the J-tube and the end of the wire binding the tin foil at the top is carried down through *B* until it makes contact with the mercury; the end of the wire at the bottom dips into the mercury in *C*. The soot coating is protected by covering with a large test-tube, which is prevented from slipping about by means of the slightly smaller glass ring *E* fastened to the paraffin. *A* and *D* form the terminals.

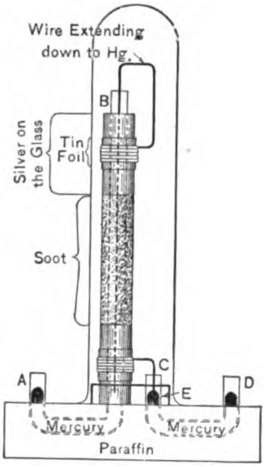

Fig. 1.

A block of wood or paraffin, into which are fastened vertically a number of glass tubes, can be conveniently used for storing a series of resistances of various magnitudes, so that when one is wanted, all that is necessary is to transfer it from the rack to the mounting.

Berlin, October 19, 1903.

NOTE.

George Gabriel Stokes. — George Gabriel Stokes was born in Ireland on August 13, 1819. His father, the Rev. Gabriel Stokes, was rector of the church in the little village of Skreen, Sligo Co., his mother being a daughter of the rector of Kilrea. He was sent for his early education to Dr. Wahl's school in Dublin and afterwards to the College in Bristol, whence in 1837 he proceeded to Cambridge, entering at Pembroke College. His life was henceforth fully identified with the interests of his college. He was elected to a fellowship just after taking his degree in 1841, and retained it until his marriage in 1857 to a daughter of the Rev. T. R. Robinson, D.D., Director of Armagh Observatory. Under the statutes of the university at that time in force, this event compelled him to vacate his fellowship, but he was reëlected in 1869 under the new statutes and only resigned in 1902, when he was 83 years old, to become Master of the College. His tenure of the latter post was short; he died on February 1, 1903.

Practically the whole of Stokes's scientific life was connected with the interests of two bodies — his University and the Royal Society. He graduated as senior wrangler in 1841, the first of the great triumvirate which attained the coveted honor in three successive years — Stokes, Cayley, Adams. There were giants in those days. Sylvester and George Green had taken their degrees in 1837 and Lord Kelvin followed in 1845, and chief amongst those of note in other lines, was Charles Kingsley, who took honors in mathematics and classics in 1842. This period was in reality not far removed from the time when British mathematics had been entirely isolated. Until the beginning of the century Newton's methods and fluxional notation were almost exclusively employed and it was only some ten years before Stokes matriculated that the influence of Woodhouse, aided later by Peacock, J. F. W. Herschel, Babbage, Whewell, Airy and others, was successful in completely establishing continental methods for examination purposes and in forcing the recognition of the mathematical work which had made such advances outside the country. Thus the men of the period, in the middle of which came Stokes, had the advantage of being trained by those who were thoroughly grounded in the old methods but who had spent time and energy in working up and introducing the new. Neither was the intellectual activity of the pioneers of the new movement confined to research in mathematics. Text-books had been written setting forth the continental methods, and translations of foreign works had been made. A classical tripos had been established in 1824, but all candidates who went in for it were required to have taken honors previously in mathematics — a rule abolished in 1850.

The mathematical power of Stokes began to show itself immediately. His first paper was published the year after he took his degree and the decade which followed was certainly the most fruitful of his life in regard to the equality and quantity of the work which has come directly from his pen. The Royal Society Catalogue contains the titles of over fifty papers printed within this period, and many of these are not only of far-reaching importance but mark the beginnings of his researches into almost every department of mathematical physics — hydrodynamics, light, elastic solids, the mathematical expression of wave motion by Fourier's series, sound and conduction of heat. Modest as he was concerning his own achievements, he thought nearly all of these papers sufficiently good to be included in his collected works, the first three volumes of which cover this period alone. To mention a few of the most important, we have the researches "On the Steady Motion of Incompressible Fluids" and "On the Theories of the Internal Friction of Fluids in Motion, and of the Equilibrium and Motion of Elastic Solids," with a "Supplement," which together constitute the complete foundation of the hydrokinetics of the present day. In the paper "On the Effect of the Internal Friction of Fluids on the Motion of Pendulums," he considers and works out the effect of viscosity on various kinds of motion. Deep sea waves and the solitary wave are very fully treated in the memoir "On the Theory of Oscillatory Waves." But the theory of light was the subject in which he seems to have been most willing to work. The two papers "On the Dynamical Theory of Diffraction," and "On the Change of Refrangibility of Light," in the latter of which fluorescence is described and explained, would have alone sufficed to make his reputation.

Two further papers, "On the Critical Values of the Sums of Periodic Series" and "On the Numerical Calculation of a Class of Definite Integrals and Infinite Series," must be mentioned, not only because of their great intrinsic value, but also because they show that the author was right abreast of the developments in pure mathematics at that time and that he was able to advance them and use them as an instrument of research for the investigation of physical problems.

This last fact is perhaps worth insisting on at the present time, when the separation between pure mathematics and physics has become far wider than is advantageous for either. The physicist works mainly in his laboratory, the mathematician at his desk, neither entrenching on the domain of the other. Even the magnificent work of Poincaré, introducing the rigorous and fruitful methods of pure mathematics for the treatment of physical problems, is only a partial step in the right direction. With Stokes this divorce never occurred; experiment went hand in hand with theory. As early as 1840 he had fitted up a small laboratory in his rooms, of simple character it is true, but none the less sufficient to test, sometimes searchingly, the results of his theories. And it was the same all through his life. He was never content to leave a theory unconfirmed by experiment, and if a new observation were made it must be compared with theory. These qualities are especially noticeable in some of his earlier papers. In that on internal friction, he explains the suspension of clouds and the subsidence of ripples and waves after a storm; in those on oscillatory wave motion, the well-known experiments of Scott Russell are fully considered; his paper on diffraction is divided into two parts consisting of his theory and of the experiments which he made to test it, and so on. Later in life he would, in a short note or a few remarks, give the main outline of an explanation of some new phenomenon; further research by others usually proved him to be correct.

This active period quickly brought recognition to him. In 1849 he succeeded to the Lucasian chair of mathematics in Cambridge, a post held previously by Isaac Barrow, Newton, Woodhouse, Airy and Babbage, and five years later he was elected secretary to the Royal Society. He was not content with delivering the two courses of lectures required of the professor by the regulations. He let it be known that he considered it part of his duty to help students in their work, and such help from a man like Stokes was not to be despised. He was always ready to give assistance, whether it was asked for work already started, or in suggesting new problems to be undertaken, or in giving encouragement where failure seemed likely. This trait was even more conspicuous during his thirty-one years' tenure of the Royal Society position. Naturally brought into contact with all the best work which was being done throughout the country, he largely gave himself up to helping others. This was undoubtedly the main reason for the smaller output after this time. As against 50 papers produced up to 1852, we find only 56 from then until the end of 1883, and many of the latter consist of addresses and short notes on such subjects as chemistry, details of instruments, and history of science, all valuable but perhaps not epoch-making like the earlier memoirs. His reward was the frequent acknowledgment of his assistance which those alone who had received knew how to appreciate. A generous tribute is given by Lord Kelvin[1] of his own indebtedness, and a further one by an anonymous writer,[2] who tells that though he was previously quite unknown, some work of his attracted the attention of Stokes and a correspondence was started in the course of which on one particular day he received as many as three letters and a telegram! It is unnecessary to say a word on the quality of the assistance given. It was the same throughout; knowledge and time were always at the disposal of small and great.

---

[1] Nature, February 12, 1903.

[2] *Ibid.*, February 19, 1903.

It has been said that much of Stokes's work was given to others, and indeed some of it was never published in scientific journals at all. An instance of this occurs with reference to the transformation of a line integral into a surface integral which he put as a question in a Smith's prize examination paper in 1854. Again, he had thought out the physical basis of the solar spectrum some seven years before Kirchhoff, and had been in the habit of lecturing on it. Stokes deprecated any attempt to obtain for himself the credit of this discovery, saying that he had failed to take an essential step in the process. It is possible that the papers he left behind will tell even more of his own work than we know now, and they will doubtless add much to the scientific history of the second half of the last century.

Amongst other honors, Stokes received the Rumford medal in 1852, the Copley medal in 1893, was Burnett Lecturer 1883–5, Gifford Lecturer 1890–2, and was created a baronet in 1889 when Lord Salisbury was prime minister.

In 1885, Stokes received the highest scientific honor which England has to bestow — the Presidency of the Royal Society; this he held until 1890. From 1887–1892 he represented the University in Parliament. Being still Lucasian Professor, he thus attained the unique distinction of holding the three positions simultaneously. Only once before had one man, Isaac Newton, occupied them all, and in his case the tenures were at different periods of his life. In 1899, Cambridge University fittingly celebrated the jubilee of his election as professor, inviting representatives from all parts of the world and publishing a memorial volume of the Transactions of the Cambridge Philosophical Society a body to which many of his papers had been communicated. Although at this time about to enter his eighty-first year, he seemed able to endure fatigue without showing signs of his advanced age. On the chief day set apart by the university, he attended morning and afternoon congregations of the senate, a lunch, and a late banquet, and the following day was early in London to attend a committee, only closing his labors on various matters late that night.

A word must be said concerning Stokes's relation to religious questions, partly because they evidently entered much into his thoughts and formed an essential part of his character, and partly because during the last twenty years of his life there were published addresses and papers on the question by him. On several occasions he spoke before the

Church Congress, the Victoria Institute and other bodies on the relation between science and faith. What value is to be set on these, this is not the place to discuss; it is sufficient to mention that he took a prominent part in the efforts made in England in educating the public to higher views of the relations of science to theology, and in rescuing the study of the former from the doubtful position which it had, even among some of the more advanced students of religious questions. His own personality and the methods of treatment which he adopted were always on the side of promoting good feeling and tending towards the prevention of acrimonious discussion amongst those whose opinions differed most widely. He avoided, as a rule, dogmatic statements and treated the questions in his usual scientific manner, allowing his own opinions to be inferred rather than expressly stated.

The published portraits of Stokes, representing him with a somewhat severe type of countenance, fail to bring out a characteristic expression. Ordinarily silent in society, he would freely talk on any subject that interested him. While telling of some remarkable fact or observation, the broad high forehead would pucker into a thousand wrinkles and a smile would light up his face with a brilliancy which seemed to show a concentrated picture of the whole man. Those who had the privilege of listening to his highly-finished and carefully worded lectures on the wave-theory of light delivered without a note, or of watching the simple experiments and diagrams with which he illustrated them, will remember how eagerly they looked for the first symptoms of this change. The lectures, too, were characteristic. Toward the end of the course, evidently wishing to give more than was possible in the limited time, he would continue further and further over the allotted hour until the last day when, on one occasion, amid the gradual disappearance of the class to fulfill other engagements, he kept those who remained interested for nearly three hours.

There was but little apparent failure of Stokes's physical and intellectual powers until within a few days of his death at the age of eighty-three. He died as he had lived — in harness — and a great figure passed away from the scene at the close of a well-rounded and successful career. His work, mainly on wave-motion and the tranformations which, in its different forms, it undergoes under various circumstances, has already taken a permanent place in the history of science. And he has left behind with those who knew him a memorial of himself which will not be easily effaced.

E. W. B.

NEW BOOKS.

Mineralogy. By HENRY A. MIERS. London and New York, The Macmillan Company, 1902. Pp. 584.

The limitations in the scope of this text-book are perhaps best indicated by a quotation from the preface: "The student will not find in the following pages any systematic account of the modes of occurrence of minerals, their geological distribution, their origin, their alterations, or their artificial reproductions." These topics are set aside as deserving to form a separate volume.

The matter selected for treatment in the book is taken up in two parts: I., The Properties of Minerals, and II., Description of the More Important Mineral Species. The most extensive chapters in Part I. are those dealing with "The Crystalline Form" and "The Optical Properties of Crystals." Both these topics are treated with accuracy and with a distinct originality in the method of presentation. In the opinion of the reviewer, these chapters are suited to supplement rather than to supplant the more usual styles of treatment. In the matter of obliterating the sharp distinction between the conceptions *crystal* and *mineral*, which should exist in the mind of the student, and doubtless does exist in the mind of the author, the book bears an unfortunate similarity to many of its predecessors. In most cases emphasis is laid on actual determinations of the various physical properties of minerals by the student, and much attention is given to the apparatus and methods for making these determinations. In this respect the book is suggestive but not at all exhaustive. Especial mention might be made of the attention given to specific heat, also of the discussions upon the relations between the properties of minerals, etc.

In Part II. the aim is to describe the more common species rather fully, omitting the rarer minerals entirely. Consequently only about 250 of the 1,000 known varieties and species are mentioned. The descriptions are interesting to an unusual degree, and lay especial stress on the peculiarities which can be readily observed by the learner. The classification of species is not readily comprehensible. For instance, mica and tourmaline are placed in the section entitled "Silicates Containing Halogens," while topaz and sodalite are not included. Many such instances could be cited.

With all its lack of logical development in the arrangement of details, the book may be characterized as accurate, suggestive, original in method, and distinctly progressive in matters pertaining to crystallography. Its usefulness as a book of reference has been purposely sacrificed in order to attain greater efficiency as a text-book, yet the tables of physical properties — index of refraction, double refraction, optical angle and specific gravity — will be found helpful to many besides the beginners in mineralogy.

A word should be added with regard to the illustrations. They have in a remarkable degree the property of *illustrating*. Even in the rare instances where there are flagrant inaccuracies of execution (*e. g.*, Fig. 271), the main idea is clearly conveyed.

On the whole, this new text-book seems well adapted to improving the quality of instruction given in the subject of mineralogy.

A. C. Gill.

A Laboratory Manual of Physics. By H. C. Cheston, P. R. Dean and C. E. Timmerman. New York, American Book Co., 1902. Pp. 128.

This book, written to meet the needs of the high schools of New York, has found its way into a larger circle of readers. The experiments here described are 72 in number and are distributed as follows: To the mechanics of solids, 22; of liquids, 6; of air, 5; to sound, 3; to heat, 9; to light, 8; to electricity and magnetism, 22. Many of the exercises are identical with those found in Hall and Bergen's book. The large majority of the exercises are quantitative in character. They are aimed to meet the requirements of Harvard University; of the syllabus of the Middle States Examination Board and that of the regents of New York State. Each experiment includes a statement of the object of the exercise, the apparatus needed, directions for work, a tabular form for recording the measurements and a conclusion. The tabular forms suggesting methods of record are a very valuable feature of the book. The directions are clear, concise and logical. Experience shows that some of the exercises are too long for the time that can ordinarily be assigned to them. This is true of Ex. 5, "The relation between the weight of a displaced liquid and the loss of weight of the solid." This should be separated into two. Some experiments, *e. g.*, Ex. 9, "To determine the pressure of the air on a square centimeter of surface" would better be performed on the lecture table. Many illustrations and cuts are given and a table of physical constants and trigonometric functions is added.

R. H. Cornish.

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THE
PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE
AMERICAN PHYSICAL SOCIETY

BY
EDWARD L. NICHOLS
ERNEST MERRITT, and FREDERICK BEDELL

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FEBRUARY, 1904

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THE

PHYSICAL REVIEW.

ON THE VELOCITY OF LIGHT IN A MAGNETIC FIELD.

✓

BY JOHN MILLS.

SEVERAL investigations have at various times been undertaken to determine the nature of the Faraday "effect." The kinematical explanation of the rotation of the plane of polarization in natural rotatory substances by the assumption of two oppositely polarized circular components which travel with different velocities has led many investigators to a similar explanation in the case of a magnetic rotation of the plane of polarization. The more important of these investigations of the velocity of light in traversing a medium in an electromagnetic field are those of Messrs. Righi,[1] Brace[2] and Morley and Miller.[3] In every case the method has been to note the shifting of the interference bands formed by the divided portions of the same beam, one portion of which has traversed a medium in a magnetic field.

The investigation which is here described was performed with the apparatus granted to Messrs. Morley and Miller by the A.A.A.S. Their apparatus consisted of the more general type of a Michelson interferometer in the path of each ray of which was placed a tube of carbon bisulphide, surrounded by a coil and supported independently of the coil. The coils were differentially wound and each winding had independent terminals allowing the separate windings to be connected in series or differentially. Connecting the windings of one coil in series and those of the other differentially they obtained the same current and consequently the same heating effect in both, while only one coil acted as a solenoid. By a proper adjustment of their apparatus fringes were visible formed not only from the end mirrors of the interferometer but also two other sets one from the two glass plates covering the nearer ends of the two brass tubes and another from the plates at the further ends. Any shifting due to mechanical causes was then observable in the last two sets. A slight displacement noticeable on the making or breaking of the current circuit — but not apparent in the last two sets of fringes mentioned above, and therefore due to change in the sulphide — many times however as large as the effect suspected from the mathematical analysis of Mr. Eddy,[1] suggested a change in the density of the carbon bisulphide. Experiment failed however to detect any such change of density or volume. Using natural light from a sodium burner or sometimes interposing a Nicol prism they were unable to observe any shifting of the fringes indicating a change in velocity.

---

[1] Nuov. Cim., 3, 1878, Beibl. 2, p. 715.

[2] Wied. Ann., 26, p. 576, 1885.

[3] PHYS. REV., 7, p. 288, 1898. See also Becquerel, Compt. rend., 88, p. 334, 1879, Beibl. 4, p. 624. Cornu, Compt. rend., 99, p. 1045, 1884, Beibl. 9, p. 273.

In the present experiment two changes were made in the method. First: the light used was passed through a 1–4 λ plate after leaving the Nicol, for both Righi and Brace had noted in their researches that no shifting occurred or was to be expected for plane polarized light. Second: the chance of a shifting of the bands due to any mechanical cause was entirely eliminated by the use, instead of a single quarter wave plates of a Bravais double plate giving one half of the field of right- and the other half of left-handed circularly polarized light. The interference bands were then adjusted perpendicularly to the dividing line of the plate. Any shifting then due to mechanical causes would be in the same direction for both sets of bands; on the other hand any displacement of one half over the other would indicate a differential change in velocity. The separate windings could now be connected in series, making both coils solenoids and disregarding the mechanical effect of their juxtaposition. By these two means for the same current as before an effect of four times the magnitude was to be expected.

---

[1] Phys. Rev., 7, p. 283, 1898.

With the apparatus just described a distinct shifting of the fringes was noticed, and this shifting increased with the current. By interposing a rheostat in the system the current could be gradually increased until the shifting amounted to a full band — that is until the fringes again coincided. Then using about this same intensity of current the connection was made and the current adjusted more delicately with the rheostat until the coincidence appeared perfect. The writer observed at the telescope. The ammeter readings, however, were taken by an assistant and were not announced until the set was completed. The total drop of potential across the terminals of the system was changed after every other reading by the addition or subtraction of a portion of the storage cells used. In this way the observer was ignorant of the probable current readings for various positions of the rheostat lever arm. As the light forming the fringes had traversed in each tube some 150 centimeters of the sulphide fringes formed could not be read accurately much beyond 1–15. For example: the largest deviation from the mean in the case of one band (see Table I.) was .93 ampere, giving a sensibility of about one part in fifteen.

A more recent paper of Mr. Brace[1] has shown that the velocity of a circular ray in the direction of the amperian currents is accel-

Table I.

For a displacement of one band.

Ammeter Readings.	Corresponding Difference of Phase of the Two Circular Components.	Ammeter Readings.	Corresponding Difference of Phase of the Two Circular Components.
13.4	367.1	13.5	369.8
13.6	372.6	13.2	361.7
14.15	387.6	13.3	364.4
13.6	372.6	13.5	369.8
14	383.5	12.5	342.5
13.25	363	13.4	367.1
13.2	361.7	13.45	368.5
13.6	372.6	13.45	368.5
13.5	369.8	13.7	375.3
12.9	353.4		Mean 367.9°
13.4	367.1		

---

[1] The Observation of the Resolution of Light into its Circular Components in the Faraday Effect, *Phil. Mag.*, April, 1901, p. 464.

erated. It was assumed then that the effect observed was due to that cause. To check the results obtained with the corresponding rotation which would have been noticed in the case of plane polarized light a set of readings of the current necessary to rotate the plane of polarization 90° was taken for each coil. For one coil this value was found to be 13.06 amperes, for the other 13.23. Of these sets the mean is 13.14 amperes. The accuracy of this result is within one per cent. The current then that would be necessary in the case of a series connection to produce a shift of one band would be 13.14. In the preceding table it is to be noted that the current mentioned above with the form of apparatus used is equivalent to a rotation of the plane of polarization of 180°, that is to a difference in phase between the two circular components of 360°.

Table II.

For a displacement of three bands.

Ammeter Readings.	Corresponding Difference of Phase of the Two Circular Components.	Ammeter Readings.	Corresponding Difference of Phase of the Two Circular Components.
39	1067°	42	1150
38	1041	40.5	1110
41	1123	40	1093
39	1067	40.5	1110
39.5	1082	41	1123
40	1093	42	1150
41.5	1136	40.5	1110
40.5	1110	39	1067
40.5	1110	40	1093
39	1067		
40.5	1110		Mean 1101°

A further set of readings was taken for a larger current. The system was connected with the 500-volt power circuit of the local traction company. A water rheostat was used and both the rheostat and ammeter manipulated by an independent observer. The current was increased until the writer had counted three full bands; upon the coincidence of the third the ammeter reading was taken at his call. The current was then still further increased until the coincidence was no longer perfect and decreased at the observer's call until the coincidence of the third band again seemed perfect; at this point another ammeter reading was taken. Owing to the rapidly changing current due to the heating effect on the coils and the rheostat the ammeter readings could not be taken more accurately than within two per cent. There was lacking as well the deliberation of setting possible for a smaller current, as the fringes formed were quickly susceptible to changes. A difference of one tenth of a band was easily observable, however. In general only one or two readings could be taken at a time. The coils were then allowed to cool before the next reading.

A shifting of four bands was noticed for a current of some 52 amperes, but the heating effects of such a large current made it impossible to obtain a set of readings for that displacement with the same degree of accuracy as was possible in the preceding sets.

The writer was unable to detect any asymmetry in the amount of acceleration of one component as compared to the corresponding retardation of the other. A cross hair was used in the observing telescope and the two sets of fringes were observed to shift symmetrically with respect to it.

The experiment just described was undertaken at the suggestion of Dr. D. B. Brace to whom the writer wishes to express his thanks for his interest.

PHYSICAL LABORATORY, UNIVERSITY OF NEBRASKA, LINCOLN,
August 6, 1903.

A HALF-SHADE ELLIPTICAL POLARIZER AND COMPENSATOR.

By D. B. Brace.

FRESNEL[1] has shown that the intensity of a beam of polarized light of unit amplitude, after passing through two double refracting plates and an analyzing nicol is given by the formula.

$$\begin{aligned}\cos^2 s &+ \sin 2i' \sin 2a \cos 2(a+i'-s) \sin^2 \pi N' \\ &- \cos 2i' \sin 2a \sin 2(a+i'-s) \sin^2 \pi N \\ &- \sin 2i' \cos^2 a \sin 2(a+i'-s) \sin^2 \pi(N'+N) \\ &+ \sin 2i' \sin^2 a \sin 2(a+i'-s) \sin^2 \pi(N'-N)\end{aligned} \qquad (1)$$

where the primes refer to the first plate, s is the azimuth of the final with the initial plane of vibration, i' the azimuth of the principal component of vibration in the first plate, a the azimuth of the principal vibration in the second plate with that of the first and N the differential order of the double refraction of the plates. If instead of a first plate of uniform thickness we suppose two in juxtaposition of different thicknesses but in the same azimuth, then, if the nicols are crossed, we have, as the condition for a match, since

$$s = 90^\circ \text{ and } i' = i'',$$

$$\begin{aligned}&- \sin 2i' \sin 2a \cos 2(a+i') \sin^2 \pi N' \\ &\qquad + \cos 2i' \sin 2a \sin 2(a+i') \sin^2 \pi N \\ &+ \sin 2i' \cos^2 a \sin 2(a+i') \sin^2 \pi(N'+N) \\ &\qquad - \sin 2i' \sin^2 a \sin 2(a+i') \sin^2 \pi(N'-N) \\ = &- \sin 2i' \sin 2a \cos 2(a+i') \sin^2 \pi N'' \\ &\qquad + \cos 2i' \sin 2a \sin 2(a+i') \sin^2 \pi N \\ &+ \sin 2i' \cos^2 a \sin 2(a+i') \sin^2 \pi(N''+N) \\ &\qquad - \sin 2i' \sin^2 a \sin 2(a+i') \sin^2 \pi(N''-N)\end{aligned} \qquad (2)$$

---

[1] Oeuvres, T. 1, p. 624.

If i is the azimuth of the second plate $a = i - i'$. Substituting, the first term becomes

$$
\begin{aligned}
&- \sin 2i' \sin 2(i - i') \cos 2i \sin^2 \pi N' \\
&\qquad\qquad + \cos 2i' \sin 2(i - i') \sin 2i \sin^2 \pi N \\
&+ \sin 2i' \cos^2(i - i') \sin 2i \sin^2 \pi(N' + N) \\
&\qquad\qquad - \sin 2i' \sin^2 (i - i') \sin 2i \sin^2 \pi(N' - N).
\end{aligned}
$$

If now the plates are interchanged the intensity of the light will not be affected since, on interchanging the primes, we have

$$
\begin{aligned}
&- \sin 2i \sin - 2(i - i') \cos 2i' \sin^2 \pi N \\
&\qquad + \cos 2i \sin - 2(i - i') \sin 2i' \sin^2 \pi N' \\
&+ \sin 2i \cos^2 - (i - i') \sin 2i' \sin^2 \pi(N' + N) \\
&\qquad - \sin 2i \sin^2 - (i - i') \sin 2i' \sin^2 - (N' - N),
\end{aligned}
\tag{2a}
$$

which is identical with the previous expression. The same will be true of the second member of (2). Hence the consequences to be deduced will be independent of the order of succession of the plates.

Expanding in (2) the sine and cosine, transposing and substituting $\sin^2 x - \sin^2 y = \sin(x + y) \sin(x - y)$ and dividing through by $\sin 2i'$ and $\sin \pi (N' - N'')$, since neither will be zero in our applications, we have

$$
\begin{aligned}
&(- \cos 2i' \sin 2a \cos 2a + \sin 2i' \sin^2 2a) \sin \pi (N' + N'') \\
&\qquad + (\cos 2i' \cos^2 a \sin 2a \\
&\quad + \sin 2i' \cos^2 a \cos 2a) \sin \pi (N' + N'' + 2N) \\
&+ (- \cos 2i' \sin^2 a \sin 2a - \sin 2i' \sin^2 a \cos 2a) \sin \pi (N' \\
&\qquad + N'' - 2N) = 0.
\end{aligned}
\tag{3}
$$

In order to discuss the roots of this equation we will transform to the tangent form since it may take any value between $+\infty$ and $-\infty$. Substituting,

$$
\sin 2a = \frac{2 \tan a}{1 + \tan^2 a}, \qquad \sin^2 a = \frac{\tan^2 a}{1 + \tan^2 a},
$$

$$
\cos 2a = \frac{1 - \tan^2 a}{1 + \tan^2 a}, \qquad \cos^2 a = \frac{1}{1 + \tan^2 a}.
$$

and collecting terms, we have

$$\begin{aligned}
&\tan^4 a\{-\sin 2i' \sin \pi[2N-(N'+N'')]\}\\
&+\tan^3 a\{2\cos i' \sin \pi(N'+N'')+2\cos 2i' \sin \pi[2N-(N'+N'')]\}\\
&+\tan^2 a\{4\sin 2i' \sin \pi(N'+N'')-\sin 2i' \sin \pi(2N+N'+N'')\\
&\qquad\qquad+\sin 2i' \sin \pi[2N-(N'+N'')]\}\\
&+\tan a\{-2\cos 2i' \sin \pi(N'+N'')+2\cos 2i' \sin \pi(2N+N'+N'')\},\\
&\qquad+\{\sin 2i' \sin \pi(2N+N'+N'')\}=0. \qquad (5)
\end{aligned}$$

Dividing through by the coefficient of $\tan^4 a$ we see that the constant term is

$$-\frac{\sin \pi[2N-(N'+N'')]}{\sin \pi[2N+(N'+N'')]}.$$

In the physical applications the second plate and the mean of the first two will never be of a higher order than a quarter wave. We will, therefore, discuss the roots of this equation under the conditions that

$$N \ngtr \tfrac{1}{4}, \text{ and } 2N+N'+N'' \ngtr 1. \qquad (6)$$

The numerator of the constant term is positive and the denominator is positive, when $2N > N'+N''$, and thus, under the assumed conditions, this term is negative, and hence we know by the rule of signs that there are at least two real roots, one positive and the other negative, *i. e.*, we can always obtain a match in two different positions of the compensator. Thus, if we set the biplate in any azimuth whatever, we can always rotate the compensator into two positions that will give a match, and that too for any color of the spectrum which satisfies (6). If we make either N' or $N''=0$ we see that these conditions are not changed. In this case our biplate reduces to a plate of uniform thickness. This plate may cover one half the field of view or form a single strip — a "sensitive-strip" — for furnishing a sensitive system of comparison. Whatever its position, the compensator can always be set for a match in two positions for any color. For most purposes it will be preferable (for reasons given later) to set the biplate or strip in the position of greatest intensity, namely, at an azimuth of 45°.

Introducing the condition $i' = i'' = 45^\circ$, the biquadratic reduces to the form

$$\begin{aligned}\tan^4 a\{-\sin\pi[2N-(N'+N'')]\} + \tan^2 a\{4\sin\pi(N'+N'') \\ -\sin\pi[2N+(N'+N'')] + \sin[2N-(N'+N'')]\} \\ + \sin\pi(2N+N'+N'') = 0.\end{aligned} \tag{7}$$

Put $A = \sin\pi[2N-(N'+N'')]$

$$\begin{aligned}B &= 4\sin\pi(N'+N'') - \sin\pi(2N+N'+N'') \\ &\qquad + \sin\pi[2N-(N'+N'')]\\ C &= \sin\pi(2N+N'+N'').\end{aligned}$$

Solving,

$$\tan^2 a = -\frac{B \pm \sqrt{\Delta}}{2A}, \tag{8}$$

where the discriminant is

$$\Delta = B^2 + 4AC.$$

If we assume the condition $2N + N' + N'' \ngtr 1$, C will always be positive. If now $2N > N' + N''$, A will always be positive and hence Δ also. Tan² a will then have two real roots. Since in this case $\Delta > B^2$, one of the roots will be positive and the other negative. Tan a itself will then have two imaginary roots and two equal real roots of opposite signs and hence a will have equal and opposite values. Thus there will be two settings of the compensator, in equal and opposite azimuths with respect to the first plate. It is needless to state that a rotation of the compensator through 180° will give the same settings. If now $2N < N' + N''$, A is $-$ and $\Delta < B^2$ and hence $\tan^2 a$ has two negative roots and consequently all the roots of tan a are imaginary and a impossible, *i. e.*, no position of the compensator will give a match. Thus if N be ever so little less than $(N' + N'')/2$ the physical problem will be impossible. When $2N = N' + N''$ one value of $\tan^2 a$ is $0/0$, and will be found to be negative on taking the variation of the functions in the usual way, and the other is $+\infty$ and hence $\tan a = \pm\infty$ or $a = \pm 90^\circ$. As $(N' + N'')/2$ decreases from the value N to 0, B approaches 0 and Δ therefore $4A^2$ so that in the limit $\tan^2 a = \pm 1$ and $a =$ becomes $\pm 45^\circ$. Hence a may have any value between $\pm 90^\circ$ and $\pm 45^\circ$ under the conditions stated. When $a = 45^\circ$ the principal axis of the compensator lies in the plane of vibration and consequently produces no effect. Between these limits we have all the settings requisite for obtaining a match in any case of double refraction whatever. In the case $2N = N' + N'' = N'$ where $N'' = 0$, say, the plates are "crossed" and the equivalent thickness of the two plates is equal to that of the second plate, but rotated through an angle of 90°.

The sensibility of this system will depend, as in any photometric comparison, upon the uniformity of the intensity of the light in different portions of the field and upon the vanishing of the bounding lines when the intensities are the same. The first condition requires absolute uniformity in thickness and parallelism in the section, as well as constant angles of incidence for all rays. The second condition will be realized in proportion as the section is thinner. Hence this cannot exceed a certain limit nor can it be less than a certain amount in order that the expression for the intensity of the transmitted beam, discussed above, be great enough to ensure the greatest sensibility to the eye in judging of a match. The thickness of course will depend upon the requirements of the individual experiments, being conditioned by the available light, the absorption, reflection, etc., of the various arrangements. We may, however, reach an approximate estimate of the possibilities of such a system, where these factors do not seriously enter in, by comparison with data which we have in the case of the half-shade polariscope and the spectrophotometer.

With white light and a sensitive viewing screen with a vanishing line, settings can be made whose greatest difference will not exceed one half of one per cent. Moore[1] has attained this sensibility in the case of monochromatic light with a spectrophotometer for the mean spectral colors. With the half-shade polariscope and the use of a broad source of white light, without rotation, a setting to a thousandth of one degree is claimed. This however is never possible in practice where rotation occurs, which usually reduces the sensibility ten times or so, depending on conditions of light intensity, rotary dispersion, etc. Bates[2] has, however, attained with a sensitive-strip spectropolariscope a sensibility such that, for the mean colors of the spectrum under rotary dispersion, the extreme differences of his readings were less than .007°. To express these results photometrically, it will be necessary to obtain a change in intensity represented by this quantity. In the half-shade system, we usually have two portions of the field whose planes of polarization make a slight angle 2θ with each other. If the intensity of the light from each portion is unity, the amount passing through the analyzer for a match, is

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[1] PHYS. REV., Vol. 12, p. 161.

[2] Ann. d. Physik. (4), B. 12, p. 1096.

$$I = \sin^2 \theta. \tag{9}$$

The total change in I by a change $\delta\theta$ is

$$\delta I = 2 \sin \theta \cos \theta \delta\theta = 2\theta\delta\theta,$$

when θ is small as is usually the case.

The ratio of this to the original amount is

$$\frac{\delta I}{I} = \frac{2 \sin \theta \cos \theta \delta\theta}{\sin^2 \theta} = \frac{2\delta\theta}{\tan \theta} = 2\frac{\delta\theta}{\theta}.$$

This is the fractional change in one portion of the field and $-\delta I/I$ in the other produced by a rotation $\delta\theta$ and hence the relative change is

$$\frac{\delta I}{I} = 4\frac{\delta\theta}{\theta}. \tag{10}$$

Comparing this with our sensibiltty .005 in photometric comparisons we have

$$4\frac{\delta\theta}{\theta} \nless .005. \tag{11}$$

In the most favorable case mentioned $\delta\theta = .001°$. Hence, $4 \times 0.001° \div \theta \nless .005$ or $\theta \ngtr .8°$ and $2\theta \ngtr 1.6°$ must be the angle between the elements of the half-shade. The corresponding intensity of the field must be sufficient to give the eye the requisite degree of sensibility. This is rarely the case. However in polariscopic work it is not so much a question of specific photometric requirements as a maximum sensibility in testing rotations under given conditions. More usually where rotation occurs, $\delta\theta \ngtr .01°$.

Thus $$4\frac{0.01}{\theta} \nless .005 \text{ or } \theta \ngtr 8° \text{ or } 2\theta \ngtr 16°.$$

This value of θ will usually make the intensity of the field such that the photometric sensibility of .005 may be attained. However, even with such a sufficient source, the scattered light from the polarizer may prevent its attainment. In the experiments of Bates

$$2\theta = 20.4', \ \delta\theta = .005^\circ,$$

approximately.

Thus
$$4\frac{\delta\theta}{\theta} = 4\frac{0.3'}{10.2'} = .117,$$

or about one twenty-third the normal light sensibility, and yet this was the photometric requisite to give him the highest rotary sensibility with the available light intensity. These results will serve for comparison with those obtained from elliptic polarization with half-shade systems, the photometric and polariscopic conditions of which are practically identical.

For the sake of simplicity, let us consider — what will usually be the most effective system in practice — the first plate of uniform thickness and consisting either of a strip in the middle of the field of view or covering one side of it. Let its azimuth be 45°. Then the second member of (2) becomes, on making the substitutions, $N' = 0$, $2i' = 90^\circ$, $\theta = a - 45^\circ$ where θ is the azimuth of the second plate with the plane of vibration.

$$\begin{aligned} I &= (\sin^2 a - \cos^2 a) \cos 2a \sin^2 \pi N = \cos^2 2a \sin^2 \pi N \\ &= \sin^2 2\theta \sin^2 \pi N \qquad (12) \\ \therefore\ \delta I &= 4 \sin 2\theta \cos 2\theta \sin^2 \pi N \delta\theta. \end{aligned}$$

Hence
$$\frac{\delta I}{I} = \frac{4 \sin 2\theta \cos 2\theta \sin^2 \pi N}{\sin^2 2\theta \sin^2 \pi N} \delta\theta = 4\frac{\delta\theta}{\tan 2\theta} = 2\frac{\delta\theta}{\theta} \qquad (13)$$

when θ is small.

To determine the corresponding change in the other portion it would be necessary to differentiate the first member of (2) and then substitute the roots of the biquadratic (7). This would give too complicated an expression for interpretation; but we may obtain an approximate solution in a different way. Let x and y, $\sin\theta$ and $\cos\theta$ be the component vibrations and amplitudes. The resulting elliptical vibration referred to its center, is

$$\frac{x^2}{\sin^2\theta}+\frac{y^2}{\cos\theta^2}-\frac{2xy}{\sin\theta\cos\theta}\cos 2\pi N=\sin^2 2\pi N. \qquad (14)$$

In the first plate $i'=45°$, and $\cos^2\theta=\sin^2\theta$ and hence the axes of the vibration make an angle of 45° with the axis of the crystal. Since $N' \ngtr \frac{1}{4}$ the major axis is parallel to initial direction of vibration. The ratio of the semi-minor axis to the semi-major axis is

$$\frac{a}{b}=\sqrt{\frac{1-\cos 2\pi N'}{1+\cos 2\pi N'}}=\tan\pi N'. \qquad (16)$$

If we rotate the coördinate axes in (14) through an angle δ and equate the coefficients of xy to zero, we have

$$\tan 2\delta=\cos 2\pi N\tan 2\theta, \qquad (17)$$

which gives the angle between the y-axis and the major axis of the ellipse.

Equation (17) shows that if $N=1/4$, $\delta=0$, that is the major axis always coincides with the y-axis of the crystal. Thus if we rotate the plate from azimuth 45° to 0°, the axes of the ellipse move through the same angle. If $0<N<\frac{1}{4}$, $\delta=45°$ for $\theta=45°$, that is the major axis of the ellipse lies in the plane of vibration. If $0<\theta<45°$ the major axis will lie between the y-axis or the principal axis of the plate and the plane of the initial vibration when it is rotated. If N is small the azimuth of the major axis will remain zero as the plate is rotated and we may use (16) for the approximate ratio of the axes. Within this limit, such a plate is equivalent in its different azimuths to plates of corresponding orders in zero azimuth. The ratio of the axes of an elliptical vibration is by (16) $\tan\pi N$. When $N=1/4$ this ratio is

$$\frac{\sin\theta}{\cos\theta}=\tan\theta=\tan\pi N \text{ or } N_1=\frac{\theta}{\pi} \qquad (18)$$

when θ is small, where N_1 is the equivalent order in azimuth θ. N_1 is the equivalent order of a quarter-wave plate corresponding to a plate in zero azimuth. From (16)

$$\frac{a_1'}{b_1'}:\frac{a_1}{b_1}=\pi N_1':\pi N_1,$$

but for the same azimuth

$$\frac{a_1'}{a_1} = \frac{N'}{N},$$

and therefore

$$\frac{N_1'}{N_1} = \frac{N'}{N};$$

but

$$N_1 = \frac{\theta'}{\pi},$$

and thus

$$N_1' = \frac{\theta'}{\pi} \frac{N'}{N}, \tag{19}$$

and hence if

$$N_2 = \frac{\theta}{\pi} = N_1',$$

$$\frac{\theta}{\theta'} = \frac{N'}{N} = \frac{N_1'}{N_1}. \tag{19a}$$

In practice it is convenient to use a compensating plate of low order, say $N_1 < \frac{1}{60}$ and then an auxiliary quarter-wave plate for greater retardations, so that the approximate equations (18), (19) and (19*a*) can be used. This plate should really be of the order $\frac{1}{4}$ for the shortest waves required and then its order, for any other wave-length used, determined by means of differential dispersion after the method of channeled spectra[1] and then by means of equations (19) and (19*a*).

Returning now to the discussion of (12) and (13), it had already been shown from (8) that when $2N = N' + N''$, or when

$$N = \frac{N'}{2},$$

in the present case, there was a match and the plates were "crossed." Thus for a match the combination must be equivalent to a "crossed" system of equal order.

Equation (13) shows that, for the portion of the field covered by the second plate only, a positive increment in θ gives a positive increment in I. Since now we have shown that the two plates covering the outer portion of the field are equivalent to the first plate "crossed" (or turned through 90°), to maintain the match we must suppose the equivalent system turned in the opposite direction through an angle $-\delta\theta$, so that for the second portion of the field

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[1] Phil. Mag., Oct., 1899. Also Rendtorff, Phil. Mag., May, 1901.

$$\frac{\delta I}{I} = -2\frac{\delta\theta}{\theta} \qquad (13a)$$

approximately. If now a system of unknown order be inserted, at an azimuth of 45° in the path of the ray causing N or $\sin \pi N$ to change, a variation of $\sin 2\theta$, or of 2θ, when small, in inverse ratio will compensate the effect and I will be kept constant and the match maintained. The phase change may be obtained by noting the rotation of the compensator and calculating from (18) or (19), knowing the constants of the system.

The restriction in the use of the compensator within the limits of the optical sensibility of 1/200 or within whatever fractional change the eye can detect under the particular conditions imposed upon the system, can be calculated from (12). Thus if the order of the unknown plate is N_2 and such that $\sin^2 \pi N_2 = \sin^2 2\theta \sin^2 \pi N$ so that the match is not disturbed, the error will be in taking 2θ in place of $\sin 2\theta$. The error may be obtained by expanding the sine, which gives

$$4\theta^2 - \sin^2 2\theta = \tfrac{16}{3}\theta^4 + . \qquad (20)$$

But

$$\tfrac{16}{3}\theta^4 \div 4\theta^2 \ngtr \tfrac{1}{200}, \therefore \theta^2 \ngtr .00375 \quad \text{or} \quad \theta \ngtr 3.5^\circ$$

approximately. If the sensibility is $\frac{1}{50}$, $\theta^2 \ngtr .015$ or $\theta \ngtr 9^\circ$ approximately. This range of the compensator may be slightly different on account of the presence of the second plate, but is independent of the order of the compensating plate. For large orders of the unknown plate the sine must be used instead of the angle.

From (13) and (13a) we obtain as the relative change of intensity

$$\frac{\delta I}{I} = 4\frac{\delta\theta}{\theta}, \qquad (21)$$

which is the same as (10), the equation of the half-shade polariscope. Thus if 1/200 is the sensibility of the eye

$$4\frac{\delta\theta}{\theta} \nless .005.$$

When θ is small we have from (18) and (19)

$$\frac{\delta I}{I} = 4\frac{\delta\theta}{\theta} = 4\frac{\delta N_1}{N_1} \nless .005. \tag{22}$$

Hence the sensibility will depend upon how small a value of N_1 may be used and still give sufficient intensity for the maximum sensibility of the eye; and the availability of this value in practice will also be restricted by the mechanical and optical conditions. Sections have been obtained of order 1/700 for green light, but it is doubtful if sections of any natural double refracting material can be obtained of an order much less than 1/1,000. With direct sun light the intensity is sufficient for comparisons. Assuming this value of N' for the first plate or strip, the equivalent order of the compensating plate would be $N_1 = .0005$. Hence we have

$$4\frac{\delta N_1}{.0005} \nless .005 \text{ or } \delta N_1 \nless 6.2 \times 10^{-7} \tag{23}$$

as the limiting value of the change of phase, which could be observed under the most favorable conditions with an azimuth of 45°. If the azimuth of the strip is diminished this limit of sensibility may also be increased indefinitely; but for reasons given further on the photometric conditions are not maintained and it is doubtful if this sensibility could be increased. This is about fifty times greater than has been obtained with this same system using plates about ten times as thick, but even this latter is far beyond that of other methods heretofore used. We may compare the intensity of light in this system with that which has been found practicable in the polariscope. In the polariscope (9) gave

$$I = \sin^2\theta.$$

In this system

$$I = \sin^2 2\theta \sin^2 \pi N_1 = \sin^2 \pi N_1,$$

since

$$\theta = 45°.$$

In the experiments of Bates

$$\theta = 10.2' \text{ and } I = \sin^2 10.2'.$$

In the present instance

$$N_1 = .0005 \text{ and } \pi N_1 = 5.4',$$

and we have

$$I = \sin^2 5.4'.$$

This shows that with proper refinements in the optical system, monochromatic light can be used with this order ($N_1 = .0005$) which is also about the limit of the crystalline sections. Of the most available crystals — Iceland spar, quartz, selenite and mica — the latter is the only one from which such thin sections can be obtained. In spar $N = 300$ for 1 mm. thickness approximately, and hence for $N' = .001$ the thickness would have to be .000003 mm., and this thickness could not vary by more than .005/4 of itself to give uniform intensity over the field. This of course is utterly unattainable by any process of grinding. For quartz and selenite $N = 15$ for 1 mm. approximately. The thickness here could be twenty times as great, but this is about the limit of correction alone in a "flat" several millimeters thick. The cleavage of selenite to this degree has not thus far been found possible. For mica the thickness could be nearly double this value and hence its cleavage is practicable. The possibility of such a thin section was suggested to the writer several years ago in preparing the mica retardation plate used with the prism in the resolution of the Faraday "effect" into the circular components.[1] It was noticed that very small thin laminæ occasionally adhered to the section which was being split off and which gave, when observed directly with the eye, the characteristic tints in Newton's interference scale. After some weeks' attempts, sections, occasionally several square centimeters in area, could be obtained of uniform tint in the lesser orders of this scale. More usually these sections gave several tints with very sharp and almost vanishing bounding lines, exactly the optical condition required. Smaller strips were occasionally obtained giving as low as the first violet in Brücke's[2] corrected scale, or a thickness of only about .00017 mm. These films were very delicate and might have small holes in them, resulting from imperfect cleavage, which destroyed their efficiency when introduced into the field of view. These were mounted between the thinnest cover-glasses, which had been tested out for double refraction, with Canada balsam whose index was the same as the mean of that of mica and which would hence make the section practically invisible and thus give, further, a vanishing line at the boundary. These were frequently torn or were flowed out in the process of cementing on account of the impossibility of seeing them. With proper care and patience suitable compensator films and sensitive strips can readily be obtained from ordinary mica and mounted for the purposes mentioned.

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[1] Phil. Mag., April, 1901, p. 472.

[2] Pogg. Ann., B. 88, p. 363; Mascart, Optique, T. 1, p. 210.

Equation (12) gives for $\theta = 45°$, $I = \sin^2 \pi N_1$, the intensity of the incident polarized light, being taken equal to unity. If we call A^2 the intensity for any color, then ΣA^2 represents white light and we have

$$[I] = \Sigma[A^2 \sin^2 \pi N_1]. \tag{25}$$

Poisson's equation for light reflected normally from a thin plate reduces, for ordinary glass, to

$$I = \left(\frac{2\rho}{1 - \rho^2}\right)^2 A^2 \sin^2 2\pi N,$$

where N is the order of interference. For white light we have

$$[I] = \left(\frac{2\rho}{1 - \rho^2}\right)^2 \Sigma[A^2 \sin^2 2\pi N]. \tag{26}$$

Here N, the absolute order, corresponds to N_1, the differential order of double refraction of the plate. Thus a thin plate of order N will give the same tint by reflected light as a crystalline section of differential order N_1 gives by transmission with the nicols crossed. In three plates used the differential order N_1 had the values $\frac{1}{75}$, $\frac{1}{100}$, $\frac{1}{700}$ respectively; thus for the same absolute orders, the equivalent air thickness would be .0005 mm., the wave-length of green light, multiplied into these fractions or 6.7 $\mu\mu$, 5 $\mu\mu$, .7 $\mu\mu$. The lowest order in Brücke's table is 40 $\mu\mu$ = iron gray. With the very lowest orders white light may be used without obtaining any trace of coloration in the field of view. But higher orders, which, with fairly intense light, give no perceptible coloration, do show tint with increased intensity, as with sun light. On account of the tint and the greater prominence of the bounding line, thicker strips are not as satisfactory in intense light. Such strips, instead of being placed in an azimuth of 45°, may of course be rotated into a position of less azimuth and thus give an equivalence to a thinner section, but the vanishing of the line is less complete and the compensation of all colors less satisfactory. Hence it is necessary to use corresponding compensator sections and the thinnest sensitive strips possible with the available intensity of light and the conditions of greatest sensibility to the eye. Were it possible to cut these thinner crystalline sections and mount them "crossed" and in juxtaposition so as to obtain a completely vanishing line, the compensation might be more perfect and the coloration, if there be any, less evident than in the arrangement here described. But such a system seems unrealizable and in actual results far below the sensibility obtained with natural cleavage termini. These can usually be obtained sufficiently regular and straight for all comparison work. In fact, as frequently happens, sections of slightly different thickness in different portions give exactly that change in intensity in various parts of the field requisite for realizing the "contrast principle" in photometric comparisons. Thus, in a certain section, a portion was of order $\frac{1}{100}$ and another portion of order $\frac{1}{100} + \frac{1}{700}$ and so on. This occurred occasionally also in the very lowest orders. Instead of using such a section to realize "constrast" it could be mounted so as to make this bounding line the "vanishing" line of the fields to be compared, thus giving an equivalent to a sensitive-strip of order $\frac{1}{700}$ say. This, however, is not advisable if strips of this order can be obtained directly, since, as already mentioned, the thinner the section the more satisfactory the settings, because of the more complete vanishing of the bounding line and of the coloration when white light is used. If a strip were rotated from an azimuth of 45° into a less azimuth, any intensity could be obtained, but this was found not so satisfactory in color or in the vanishing line as a thinner strip of the same equivalent order.

Within certain limits, the second plate serves the double purpose of not only giving a half-shade combination with a vanishing line for making comparisons, but of compensating for any change of phase produced on the ray. For white light the thickness is restricted in the same way as the strip is limited to the first orders in Brücke's scale. Hence the compensation possible in this way is confined to the smaller orders. The method of compensation by rotating a plate in this way is also not generally applicable, even with homogeneous light, to the larger orders, since the intensity of the light is too great to obtain the highest sensibility in a setting for a match.

The sensibility attained with this system in actual practice compares very favorably indeed with other systems already in use. The highest sensibility available in each system was not attempted, but only that which could be conveniently obtained with ordinary precautions and under like conditions for each system. A support carrying the polarizing and analyzing nicols was arranged so that the various elements of the different systems to be compared could be inserted in the path of the ray. An acetylene flame placed before the polarizer was generally used to illuminate the system. Green glass could be placed in front of this for approximately homogeneous light tests. Immediately after the polarizing nicol, whose principal plane made 45° with the vertical, came the compensator, then the sensitive-strip, each mounted on a collar which fitted the tube containing the nicol. The collar of the latter carried a divided arc and that of the former a pointer. Next came a vertical graduated circle upon which could be mounted any plate to be compared, usually a quarter-wave plate. Then followed a vertical strip of crown glass 13 mm. wide and 2 mm. thick upon which was cemented a cover glass for receiving weights. Then came a horizontal glass strip with a clamp for producing flexure, and immediately in front of this a micrometer screw carrying two horizontal wires, a millimeter or two apart. Thirty to 50 centimeters beyond this came the analyzing nicol and circle and a short focus observing telescope. In this space could be inserted the various other pieces to be compared, such as quartz compensator, glass cubes, etc. The order of the quarter-wave mica plate was determined by means of a selenite wedge in the usual way and found to be of that order for green light $\lambda = .0005$ mm. approximately. With these elements thrown out of the field of view, the nicols were crossed. The sensitive-strip, compensator and quarter-wave plate were then thrown in and out successively and the reading for zero azimuth of each recorded. The sensitive-strip was then thrown in at an azimuth of 45°, then the compensator so as to give a match. Successive settings of the latter were then made on each side of this position where the eye could just detect a change in intensity at the vanishing line. This was now repeated with the green glass before the polarizer. With the particular system used a setting to within 0.1° with white and 0.2° with green light could be made. By means of (18), (19) and (19*a*) this sensibility can be expressed in terms of the relative retardation of the component rays. Thus with the sensitive-strip in an azimuth of 45° a match was obtained by means of the quarter-wave plate for $\theta = 56'$, which gives the equivalent order $N_1 = \frac{56}{60} \times \frac{1}{180} = \frac{1}{200}$ approxmimately. But it was proven that $N = \frac{1}{2}(N' + N'')$ so that here $N_1' = \frac{1}{2} N'$ or the order of the strip $N' = \frac{1}{100}$ for $\lambda = 500\mu\mu$ approximately. Replacing the quarter-wave plate by the compensating plate, setting for a match and rotating the same through 5°, and then introducing the quarter-wave plate, the latter gave a match again in azimuth 16′. Hence from (19*a*) the order of the compensator is $N = \frac{16}{800} \times \frac{1}{4} = \frac{1}{75}$ approximately. Thus the retardations corresponding to 0.1° and 0.2° on the compensator are

$\frac{0.1}{5} \times \frac{16}{60} \times \frac{\lambda}{180} = \frac{\lambda}{34{,}000} = 3 \times 10^{-5}\lambda$ and $6 \times 10^{-5}\lambda$ respectively. The former is fifty times the limit given in (23). From (22) $4\frac{\delta\theta}{\theta} \nless .005$. The azimuth of the quarter-wave plate to match the strip was $\theta = 56'$. The equivalent sensibility on this plate would be $\delta\theta = {}^\circ \times 0.1\frac{4}{75}$. Hence

$$4\frac{\delta\theta}{\theta} = 4\frac{0.4 \times 60}{75} \times \frac{1}{56} = .023$$

as against .005, the normal sensibility. This result indicates how well the optical conditions of uniformity of field and of a vanishing line are fulfilled by these thin sections of mica. Two settings of the compensator at 6.°5 and 13° corresponded to a proportionate rotation of the quarter-wave plate showing the proportionality within this range. Another section of mica which was among the thinnest obtained, gave a match with the quarter-wave plate in an azimuth of 8′. Hence the equivalent order of the quarter-wave plate was

$N_1 = \frac{8}{60} \times \frac{1}{180} = \frac{1}{1850}$, and the order of the strip $\frac{1}{675}$ approximately. In another section of two different thicknesses, a rotation of 8′ by the quarter-wave plate was necessary to pass from a match of one to the other. Hence the difference in orders was $N'' - N' = \frac{8}{60} \times \frac{2}{180} = \frac{1}{675}$ approximately. The sensibility of the method in comparison with others under similar optical conditions was readily obtained by introducing the various systems already mentioned. Bravais' "sensitive-tint" biplate when placed in the path of the ray showed a change of tint between the two halves of the field with a turn of 1° of the quarter-wave plate. This corresponds to a change of phase of $\frac{\lambda}{180}$ which is only about $\frac{1}{200}$ the sensibility obtained above with the sensitive strip system under the same conditions of illumination. Undoubtedly with a different intensity and more careful adjustment a higher sensibility could be obtained with not only Bravais' biplate but also with this system. In fact Bravais[1] with intense light could detect 0.7° rotation of the quarter-wave plate or $\frac{\lambda}{250}$.

The comparison with the shift of a black band was made by inserting the vertical strip, the horizontal strip and the micrometer already mentioned. The sensibility of this system depended on the amount of flexure and varied considerably. Thus with a flexure, such that the band was quite sharp and distinct, 500 gms. on the vertical strip gave a reading on the micrometer screw of 36, while the least shift of the screw which could be detected was 12. On reducing the flexure until the black band was hardly visible 200 gms. gave 23 divisions while 100 gave 11 divisions as near as could be observed. This represented the sensibility. With 200 gms. a match was obtained with the compensator on rotating 2.5°. Since 0.1° was the sensibility, this would correspond to 8 gms. or a sensibility 12.5 times that with the black band. Under more favorable conditions both systems would have given a greater sensibility, but this represents approximately the relative sensibility. Rayleigh,[2] using a lime-light and a black band, obtained 25 gms, as his sensibility. With crossed nicols alone, he obtained a sensibility over four times less, which would correspond to about fifty times less than that with the strip under similar conditions, a result approximately obtained by direct comparison. The compensators of the Babinet type would fail to give the sensibility of the single band obtained with the glass strip under flexure, since the bands are much narrower and sharper and hence less sensitive as shown above.

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[1] Pogg. Ann., 96, p. 402.

[2] Phil. Mag., Dec., 1902.

The method of Senarmont of using a quarter-wave plate or a Fresnel rhomb is of the same order of sensibility as the crossed nicols. Thus with green light 1,000 gms. on the vertical strip could not be detected, while the sensibility of the strip was 0.2° or 25 gms., or at least forty times greater. The double refraction in the Fresnel rhomb was so great that it could not be used with it at all to this degree of sensibility. A very slight pressure of the finger on a strip of glass at once showed marked contrast in the half shade. A fine quartz compensating wedge some 80 millimeters in length and ground very accurately from a differential order 0 up to 1 with compensating plate and wedge after the method of Soleil was found utterly useless to this degree of sensibility owing to the unavoidable double refraction in its glass mount. The application of a glass cube as a compensator under varying pressures as used by Bravais and by Wertheim is also subject to the same difficulty of initial strain. Only thin strips of glass are sufficiently free from strain to give an extended field of uniform intensity.

When the phase change is a function of the wave-length, as is usually the case, large retardations of different wave-lengths may be obtained by setting for a match and then varying the wave-length of the ray until a match again occurs for the next succeeding color and so on. This would represent a loss or a gain of half an order and, as in this way the full sensibility could be maintained and the portion of the spectrum or mean wave-length accurately determined, the error in the observations could be reduced to that calculated above.

Other methods of obtaining a vanishing line were tried without success. Thus by silvering a strip on the reflecting surface of a total reflecting prism, a vanishing line was obtained together with elliptically polarized light from the incident plane polarized light as

Fresnel and Brewster have shown. As the elliptical vibrations in each portion of the field were in the same direction but of different excentricities so that a match was possible, the changes in intensity in the two portions of the field were in the same direction, a condition contrary to a true half-shade instrument. The double refraction in the prism itself was an insurmountable difficulty.

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THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS IN METHYL ALCOHOL IN THE NEIGHBORHOOD OF THEIR CRITICAL POINTS. II.

By Charles A Kraus.

Discussion of Results.

As already stated, solutions in methyl alcohol exhibit a maximum of electrical conductivity which in round numbers, lies a hundred degrees below the critical point. This phenomenon was studied more carefully only in the case of potassium iodide and ammonium chloride. Even in these cases particular care was not observed, the results being obtained incidentally. However it will not be out of place to point out here a few facts that present themselves. The results are plotted in Fig. 2. The high value of the conductivity which these solutions possess beyond the critical point compared with that of such solutions as have been measured in sulphur dioxide and ammonia[1] is very striking. The fact impresses itself upon one that the comparison of the conducting power of different solvents by a comparison of the conductivity of their solutions at ordinary temperatures is somewhat arbitrary. The conductivity of a solution is a function of its temperature and it is difficult to say what temperatures are to be looked upon as corresponding temperatures. Certainly we should take into account the distance from the critical point, for in any particular solvent this is in a large measure determinative of the conductivity. Viewed in this light the alcohols approach water much more nearly in the conducting power of their solutions than do either sulphur dioxide or ammonia. How they would compare with other solvents which have not been particularly studied in relation to their maxima of conductivity can not now be said.

The maxima also show some characteristic relations in regard to the behavior of different dissolved substances. It will be noticed

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[1] A. Hagenbach, l. c.; P. Eversheim, l. c.

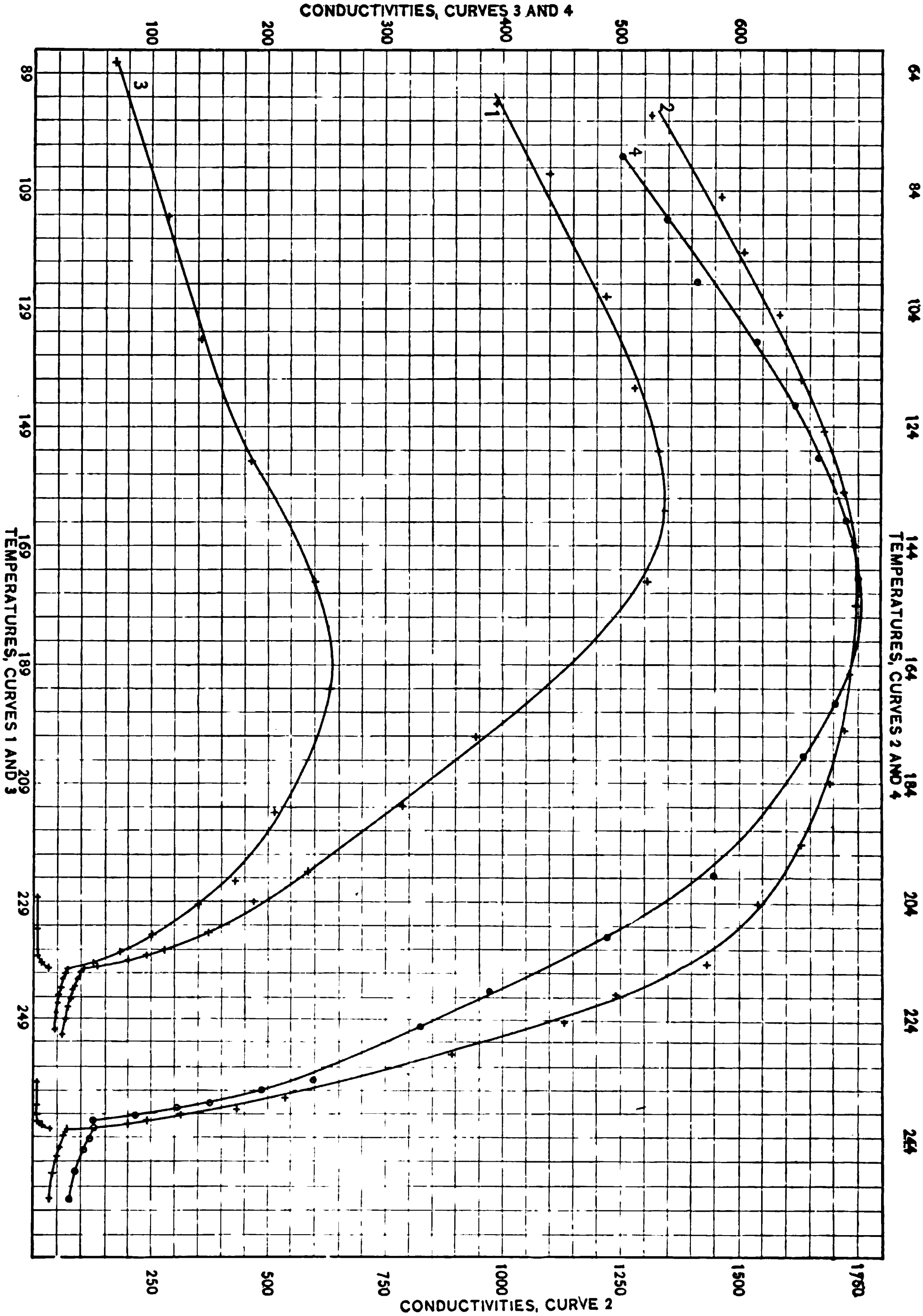
CONDUCTIVITIES, CURVES 3 AND 4
100
200
300
400
500
600
89
109
129
149
169
189
209
229
249
TEMPERATURES, CURVES 1 AND 3
64
84
104
124
144
164
184
204
224
244
TEMPERATURES, CURVES 2 AND 4
1
2
3
4
250
500
750
1000
1250
1500
1750
CONDUCTIVITIES, CURVE 2

Fig. 2.

that the curve for ammonium chloride, Curve 2, Fig. 2, much flatter than that for potassium iodide. In consulting the curves obtained by Franklin and Kraus for the same substances in ammonia it will be seen that there too the same difference exists. The relative positions of the maxima also bear much the same relations to each other in the two solvents. In the region just before the critical point is reached the ammonium chloride decreases in conductivity much more rapidly than potassium iodide. The concentration seems to have considerable influence on the position of the maxima as is apparent by comparing curves 1 and 4.

The curves studied in alcohol exhibit a constant direction of curvature until the critical point is reached, when the curvature is to the other side. The curves studied by Hagenback[1] exhibit the same peculiarity. All the curves studied by Franklin and Kraus[2] in ammonia exhibited this same behavior. Yet this is not a general property of electrolytic solutions as is seen on consulting the curve given by Franklin and Kraus[3] for potassium iodide in methylamine. In this solution the curvature turned away from the axis long before the critical temperature was reached. The curve tends to approach the axis of temperatures asymptotically. Just what would happen at the critical point in a solution of this kind it is impossible to predict. Some curves studied by Walden and Centnerszwer,[4] in sulphur dioxide exhibit the same peculiarity.

Curve 3 illustrates the reaction which takes place when a solution of potassium iodide is heated up. It is seen that already at a temperature of 140° reaction sets in, as is shown by the upward turn of the curve. Owing to this reaction the maximum lies at a much higher temperature than it otherwise would. In curve 3 the tube contained the same quantity of solute as in 1, the quantity of solvent had been somewhat diminished. In the neighborhood of 235° the reaction is complete as can be seen by comparing the values of $S \cdot V_t V \times 10^6$ in series V. and VI.

The curve between conductivity and temperature is of great interest in the immediate neighborhood of the critical point. If, as much evidence goes to show, we may have present at the critical point two molecular species;[1] then it is to be expected that the change of the conductivity will be largely influenced by the relative quantities of these species present, throughout the region in which they may exist together. A number of measurements with U-tubes, some of which were constricted at the bend, showed great differences of density, existing between different parts of the solution. As nearly as could be judged the relative density of the gaseous to the liquid portion of the tube was in the ratio of 1 to 2. It is to be borne in mind that methyl alcohol is an associated liquid, so that what applies to methyl alcohol does not necessarily apply to other liquids.

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[1] Hagenbach, l. c.

[2] Franklin and Kraus, l. c.

[3] Franklin and Kraus, l. c., p. 90.

[4] Walden and Centnerszwer, l. c., p. 555.

Indeed the work of Ramsay and Shields[2] makes it very probable that association may continue beyond the critical point. Certainly as near the critical point as we are justified in applying the formulæ, the association possesses considerable values. Whether the association is the only factor that leads to non-homogeneity beyond the critical point, or whether another factor enters such as De Heen and others have noticed in non-associated liquids may well be left an open question until the disputed points in connection with non-associated liquids have been settled. As will be shown below, solutions in methyl alcohol may be far from homogeneous beyond the critical point, if properly treated. To explain this, however, in the case of an associated liquid offers no particular difficulty and it will be unnecessary to make any further assumptions unless collateral evidence makes it desirable. The results observed by Eversheim[3] in ammonia may likewise be due to association since ammonia[4] is an associated liquid.

However, the phenomena as observed in methyl alcohol do not exhibit any essential differences from other liquids that have been investigated in this direction. Again, in the methyl alcohol there was present solute in the liquid and a certain amount of gas in the vapor. But it is to be noted in this connection that the quantities of these disturbing elements present did not give rise to any appreciable changes in the observed phenomena. In one case the vapor space was filled with hydrogen. The phenomena suffered no change. It is possible to explain the phenomena in methyl alcohol by assuming an association of the liquid, yet this does not necessarily exclude the possibility that the observed phenomena are characteristic of the change from the liquid to the gaseous state. For the present this question is best left open.

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[1] An excellent résumé of the work done in this direction together with the reference is given by J. Traube, Ann. der Phys., 8, p. 267, 1902; Traube and Teichert, Ber. d. Deut. Phys. Ges., No. 13, p. 235, 1903; E. Mathias, Jour. d. Phys., 2, p. 172, 1903.

[2] Ramsay and Shields, Zs. f. Phys. Chem., 12, p. 433, 1893.

[3] Eversheim, Phys. Zs., June 15, p. 503, 1903.

[4] Franklin and Kraus, Amer. Chem. Jour.

The differences that may arise in the tube due to different treatment as regards stirring are well illustrated by the following experiments. A tube was heated up without stirring to 0.2° below the critical point, *i. e.*, by heating the tube 0.2° higher the meniscus disappeared in the usual way. The volume occupied by the liquid at this temperature was 0.38 of the total volume of the tube. On inverting the tube once or twice the liquid disappeared entirely and an unsaturated vapor was the result. In another case the same solution was heated 3.2° above the critical point. The specific conductivity of the solution at this temperature was 94.94×10^6. The volume of the liquid at the critical point was 0.36 of the total volume of the tube.

This measurement was carried out with the solution of series XIII. In series II. the same tube was used with the same quantity of solute but with a quantity of solvent which just filled the tube at the critical point. At 3.2° above the critical point II. gave $S = 35.00 \times 10^6$. Now in the two cases we have the same quantity of solute, only in the first case the solute is contained in 0.36 of the total volume of the tube, while in the second case the solute was distributed through the entire volume of the tube. Saying that the solute in the first case was contained in 0.36 of the volume of the tube means that at the critical point the liquid occupied 0.36 of that volume and, since the volume below the critical point changed in this case but very little with the temperature, this assumption seems justified. In order to compare the conductivities in the two cases, it is necessary that the solute be distributed in the same space. If on increasing the dilution there were no change in the conductivity owing to the change in dissociation, then one might make the correction by multiplying the specific conductivity in the first case by the ratio (0.36) of the volumes in the two cases. This gives $S \cdot V_t / V \times 10^6 = 34.34$. In truth, the conductivity of alcohol solutions changes but very slowly with the dilution. Therefore the above corrected value of the conductivity in the first case should be very nearly the same as that in the second case if the properties of the solution in the first case are the same as in the second case. Now the corrected value in the first case is 34.34 against 35.00 in the second case. As regards the conductivity then, a solution, which, if properly mixed would form an unsaturated vapor solution before the critical point is reached, possesses, by virtue of non-homogeneity, arising from want of mixing, the same properties as a homogeneous solution which entirely fills the tube at the critical point. So long as the solution present be in liquid form on passing the critical point, it matters not what may be the other conditions under which it now exists; as regards the conductivity its properties are the same as those of a tube which at the critical point is homogeneously filled with liquid, provided sufficient time has not elapsed to efface the non-homogeneity by diffusion. For example, the pressure in the tube in the two cases must have been very different. The pressure then can have no considerable influence on the conductivity.[1]

On inverting the tube in series XIII. the conductivity fell to 5.2. The following may make clear what actually happened. A certain solution whose volume was 0.36 of the total volume of the tube had a specific conductivity of 94.94×10^6. If this solution was diluted with solvent which was in the liquid state as it passed the critical point, then the specific conductivity fell to 35.00 or the molecular conductivity increased in the ratio of 34.34 to 35.00 on diluting the volume of the solution from 0.36 to 1. If, on the other hand, the solution was diluted to the total volume of the tube, with solvent which was in the vapor state as the critical point was passed, then the specific conductivity fell from 94.94×10^6 to 5.2×10^6 or the molecular conductivity the dilution was decreased by the dilution in the ratio of 5.2 to 34.34. Depending therefore on whether the diluting solvent was in the liquid or the gaseous state as it passed through the critical point, at a temperature 3.2° above the critical point the molecular conductivity was increased in the ratio of 34.34 to 35.00 or it was decreased in the ratio of 34.34 to 5.2 in diluting the volume of the solution from 0.36 to 1. It is conclusively shown then that the conductivity of a solution beyond the critical point is determined in a large measure by the quantity of liquid present as the critical point was passed, the tube not having been stirred since the passing of the critical point.

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[1] Compare Hagenback, l. c., Ann. der Phys., 5, p. 305, 1901.

It still remains to determine if there is any change in the properties of either a liquid or a gas as the critical point is passed. As already pointed out this cannot be done with a tube that contains a mixture of liquidogenous and gasogenous molecules,[1] for the reason that we may have a change from one molecular species to another, a change which, in view of the different conducting power of the two species, would in all probability mask any change going on in either of the species alone. We must accordingly simplify the phenomenon by taking a tube which is as nearly as possible filled with a single species. To fill the tube with liquidogenous molecules it is only necessary to use a tube which is filled with liquid at the critical point. Series II. gives the results in such a case and the same are represented graphically in curve 9. As may be seen, the conductivity is a linear function of the temperature just below the critical point. Just beyond the critical point the conductivity is again very nearly a linear function of the temperature. It is apparent that at the critical point there is a sudden change in the tangent to the curve, indicating an abrupt change in property of the liquid as the liquid passes the critical point. In the curve plotted the conductivities are corrected for the volume. If such correction had not been made the change at the critical point would seem much greater. The question might arise if the result observed is not the result of a change brought about by the circumstance that at this point the volume ceases to change? This will indeed affect the results. The correction applied is on the basis of constant degree of dissociation. As a result of the change in volume the

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[1] In the course of the paper, when for the sake of convenience use is made of the terms liquidogenous and gasogenous molecules, it should be remembered that they are applied here to an associated liquid and that they are not necessarily identical with the same terms as applied to non-associated liquids.

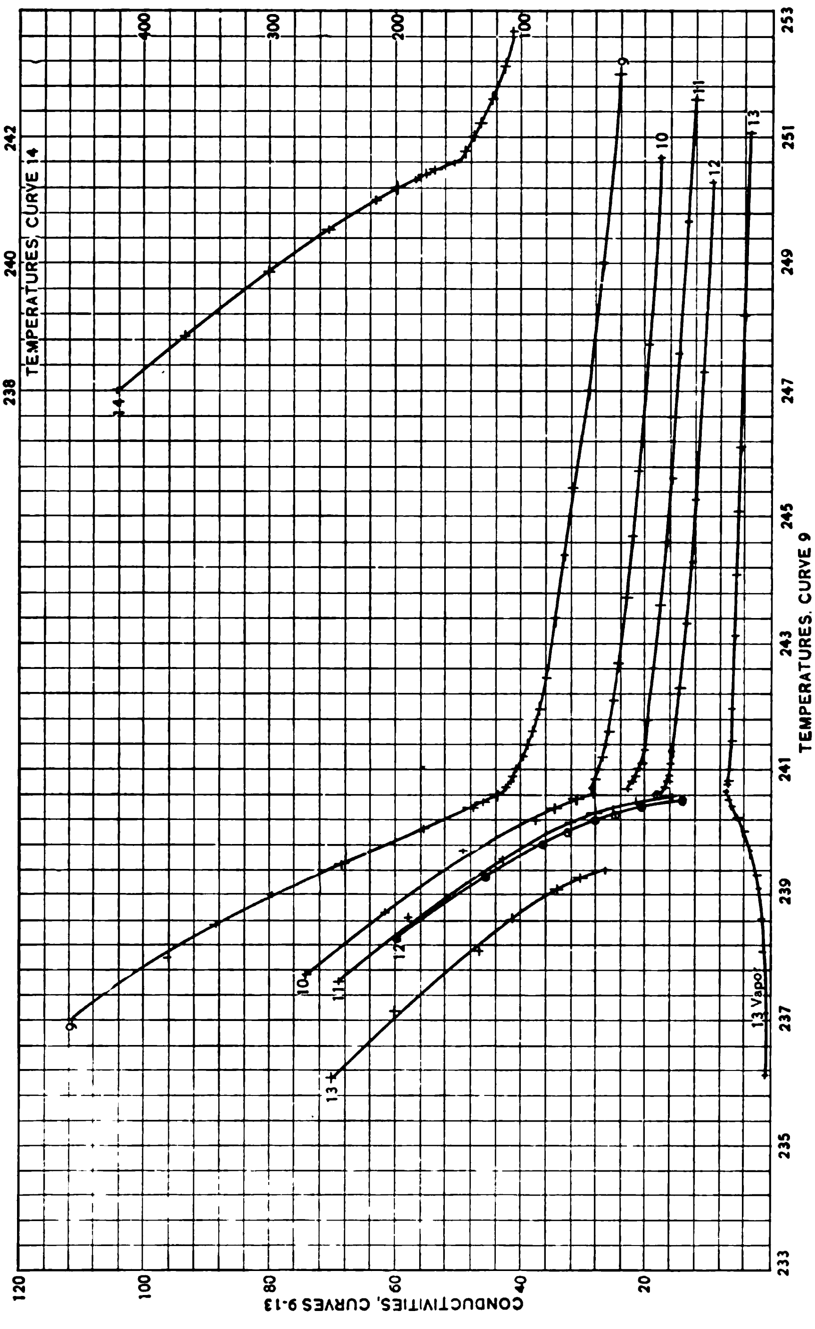
TEMPERATURES, CURVE 14
238
240
242
400
300
200
100
14
9
10
11
12
13
13 Vapor
120
100
80
60
40
20
CONDUCTIVITIES, CURVES 9-13
233
235
237
239
241
243
245
247
249
251
253
TEMPERATURES, CURVE 9

Fig. 3.

degree of dissociation is increased. The result is then that the curve as plotted, with the correction as made, will run less steep than it would if the volume and consequently the concentration had been kept constant. It seems necessary then to ascribe the change observed in the tangent to the curve to some intrinsic change in the properties of the liquid taking place at the critical point. In order to test this change further at the critical point, measurements were made on a liquid which was passed through the critical point without stirring. The results obtained in this case are those given in series XIV. and are found plotted in curve 14. The tube employed was constricted at the middle to a very small capillary in order to retard diffusion. Here again a discontinuity takes place in the tangent. No corrections were made for the change in the volume of the solution, for it is probable that the change of the liquidogenous portion of the tube continues beyond the critical point. Even with the constriction there is considerable diffusion as could be readily observed in the decrease of the conductivity, the temperature being kept constant. The result of this in the curve is to make the observed effect at the critical point less pronounced. It is to be borne in mind that the change in the volume at the critical point is very considerable. A tenth of a degree changes the volume by many per cent. In series X., curve 10, Fig. 3., the volume of the solution remained very nearly constant. The curve is in this case noticeably steeper.

To fill a tube with vapor we have merely to choose the amount of liquid such that all the liquid evaporates before the critical point is reached. Series XX., curve 20, gives the results under such conditions. The solution here evaporated 2° before the critical point was reached. No discontinuity is observable, if anything the curve runs straighter than any of the others. In series XIX. the liquid also disappeared a little below the critical point. It is again noticeable that this curve runs somewhat straighter than the curve above it. The same effect is observable in series XIII., curve 13. The liquid here disappeared at 0.2° below the critical point. It is seen then that when the tube is full of liquid at the critical point the curve beyond the critical point is comparatively straight. When the tube is about one half full of liquid at the critical point the curvature is greatest, and as the quantity of liquid at the critical point decreases the curve again becomes straighter. That the curve beyond the critical point is never quite straight is not surprising. When the tube is full of liquid at the critical point we doubtless have liquidogenous molecules breaking up into gasogenous molecules, while when the tube is filled with vapor the vapor doubtless holds a considerable number of liquidogenous molecules in solution. The breaking up, or possibly the transformation of these liquidogenous molecules into gasogenous ones has as a consequence the curvature of the conductivity-temperature curve. Whether or not the curve ever becomes parallel to the axis of temperatures as Eversheim finds for sulphur dioxide and ammonia[1] is somewhat doubtful.

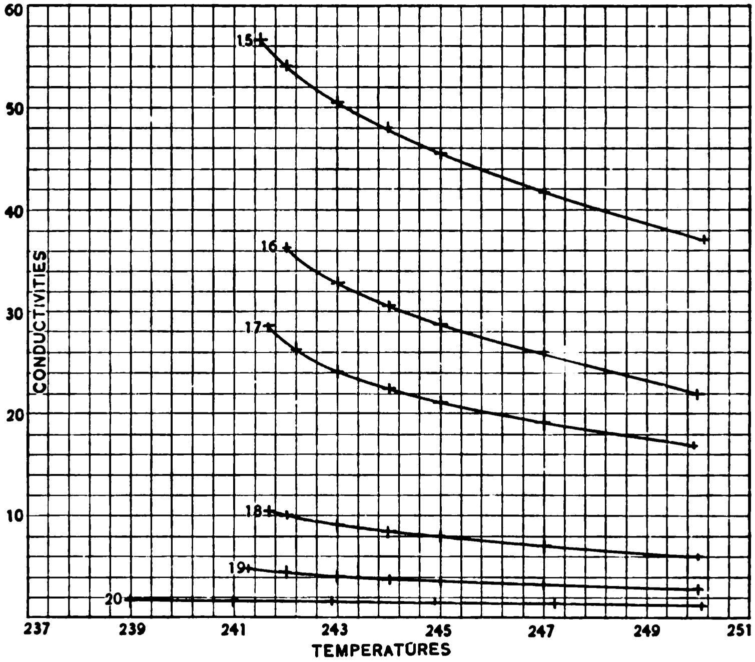

Fig. 4.

It rather seems that in the case of the alcohol solutions the curve tends to approach the axis of temperatures asymptotically. In the case of the solution which evaporated before the critical point was reached it is certainly very doubtful if there are present enough of the liquidogenous molecules to bring about the observed decrease in the value of the conductivity. It seems more probable that the change is brought about by the decrease in the dissociation of the solute consequent on the change in the molecular forces acting between solute and solvent, upon which the dissociation seems to be dependent. When we take into account the fact that electrolytic dissociation takes place as a rule only in associated liquids, and that the substances dissociated are in general capable of forming definite chemical compounds with the solvent,[1] this contention gains much strength. A case of dissociation in an unassociated liquid could be easily explained on the basis that the dissolved substance may associate itself with the solvent. The same explanation would hold true in explaining the want of dissociation of a dissociable compound in an associated liquid. Thus the acid amides are either very poor conductors or non-conductors when dissolved in water, while they are very good conductors when dissolved in ammonia. The same holds true of some other compounds such as mercuric chloride and mercuric cyanide.[2] These compounds are poor conductors in water, yet in ammonia they are relatively good conductors. At the same time the association has been shown in the case of mercuric chloride in ammonia;[3] it is probable for mercuric cyanide in ammonia. It seems possible therefore that the decrease in conductivity observed for alcohol solutions beyond the critical point is due to a change in the association factor between the solvent and the solute rather than to a breaking up of the liquidogenous molecules into gasogenous ones.

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[1] Eversheim, Phys. Zs., l. c.

Whether or not a discontinuity of the tangent takes place in the case of non-associated liquids can only be determined by experiment. If it can be shown that such change does not take place, then it will be conclusive evidence that this change in the case of methyl alcohol is due to its association. If, on the other hand, the same change takes place in non-associated liquids, then we must look upon the phenomenon as one characteristic of the change from the liquid to the gaseous state, and our views on the critical phenomenon will have to be modified, since it does not seem possible to account for a discontinuity on the basis of our present views of the critical phenomenon. The curves of Hagenback[1] show a very strong curvature at the critical point which makes it seem probable that the phenomenon in sulphur dioxide is of the same nature as in alcohol.

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[1] A. Werner, Zt. f. Anorg. Chem., 3, pp. 294–297, 1893.

[2] Franklin and Kraus, Amer. Chem. Jour., 23, p. 277, 1900.

[3] Franklin and Kraus, l. c., p. 300.

It is seen that as the critical point is approached the conductivity of the liquid falls below that of the gas just beyond the critical point — curves 10–12, Fig. 3. This is due to the loss of solute by the liquid owing to its greater concentration in the vapor. For this reason it is impossible to follow up the curve at the critical point in any case but that in which the tube is filled with liquid at the critical point. The loss of solute does not become very great except within a few tenths of a degree of the critical point. This will not affect curve 9, for the reason that at the point where the quantity of the solute in the vapor becomes appreciable, the space occupied by the vapor has become very small.

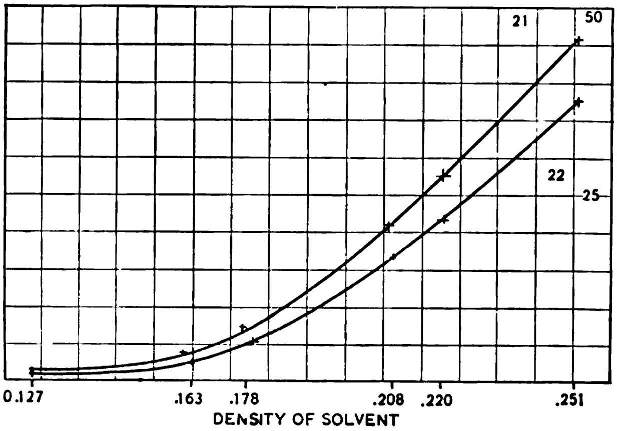

Fig. 5.

The critical state of a substance affords an excellent opportunity for studying the change of conductivity with varying density of the

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[1] A. Hagenback, l. c.

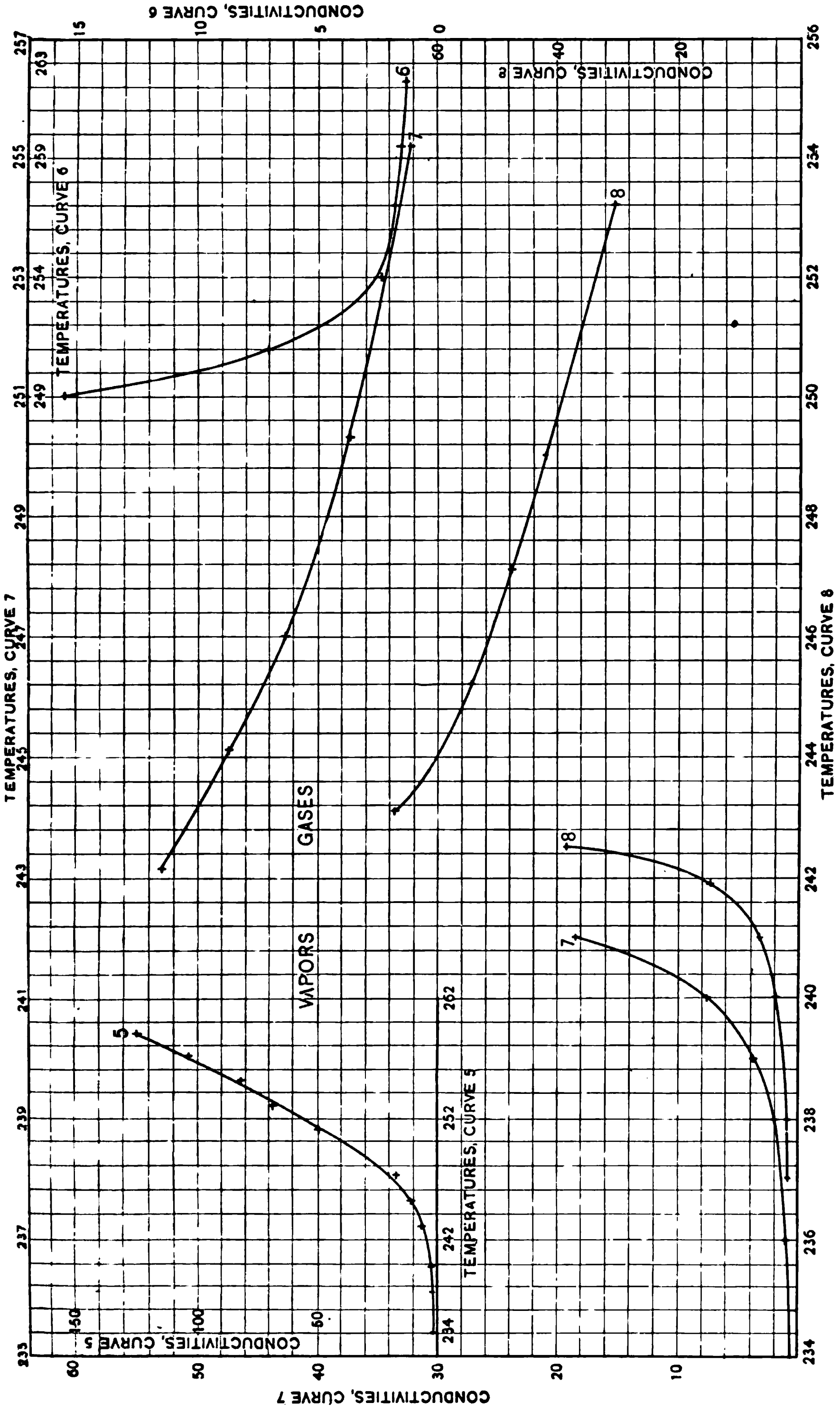
CONDUCTIVITIES, CURVE 6
15
10
5
0
CONDUCTIVITIES, CURVE 8
60
40
20
TEMPERATURES, CURVE 6
263
259
254
249
TEMPERATURES, CURVE 7
257
255
253
251
249
247
245
243
241
239
237
235
TEMPERATURES, CURVE 8
256
254
252
250
248
246
244
242
240
238
236
234
GASES
VAPORS
TEMPERATURES, CURVE 5
262
252
242
234
CONDUCTIVITIES, CURVE 5
150
100
50
CONDUCTIVITIES, CURVE 7
60
50
40
30
20
10
5
6
7
8
7
8

Fig. 6.

solvent. For this purpose the solvent was extracted from the solution as described above, leaving the solute behind. The results are given in series XV.–XX., curves 15–20, Fig. 4. The curves in Fig. 3 were originally intended for the same purpose, but a mishap rendered the concentration of the solvent somewhat inexact, and consequently the curves are useless for this particular purpose. In the case of curves 14–20 the values were obtained for the specific conductivities at 245° and 250°. These values are given in series XXI. and the results are shown graphically in curves 21 and 22 Fig. 5. For larger quantities of solvent the conductivity is very nearly proportional to the quantity of solvent. This would seem to correspond to a solution in which the solvent consists largely of liquidogenous molecules. For smaller quantities of solvent the curve approaches the axis of density of solvent. This would represent the behavior of a gasogenous solution. It is noticeable that the straight line begins to curve at a point corresponding to the density 0.180. It is at this point that the solvent disappeared at the bottom of the tube so that below this point the added solvent was present largely in gasogenous form. The effect due to added solvent becomes much more pronounced as the critical point is approached, as can be seen by comparing the two curves.

The conductivity of vapors possesses some interest. In general the conductivity of a vapor of constant concentration of both solvent and solute decreases with the temperature, as is seen from curve 20. In the case of a saturated vapor, however, the conductivity increases very rapidly as the critical point is approached. This is due to the rapid increase in the concentration of both solvent and solute. A sufficient amount of data has not yet been collected to enable the discussion of the behavior of vapors in detail. A number of curves are, however, given to illustrate their behavior (curves 5–8, Fig. 6). It is probable that curve 20 represents their behavior completely in the case of constant concentration of both solvent and solute.

SUMMARY OF RESULTS.

1. Solutions in methyl and ethyl alcohol possess maxima of electrical conductivity, the former in the neighborhood of 150°, the latter in the neighborhood of 100°.

2. Solutions in methyl and ethyl alcohol conduct beyond the critical point, the former conducting much the better.

3. The temperature coefficient of a solution in methyl alcohol undergoes a sudden change at the critical point. This phenomenon is apparent only when the tube is completely filled with liquid at the critical point, or when the solvent passes through the critical point without stirring.

4. An unsaturated vapor solution exhibits no discontinuity at the critical point of the solvent. Solutions which consist of mixtures of gasogenous and liquidogenous molecules exhibit a great change of the conductivity immediately beyond the critical point, but a discontinuity of the tangent can not be established.

5. Methyl alcohol presents the same phenomena of non-homogeneity beyond the critical point as do other liquids studied in this connection.

6. The conductivity has been studied for solutions possessing the same concentration of solute and different densities of solvent. For large quantities of solvent present the conductivity is nearly proportional to the quantity of solvent. For smaller quantities of solvent present the ratio of increase of conductivity is much smaller. As the critical point is approached, the ratio of increase of conductivity with increase of solvent is increased.

7. The vapor of a solvent may become a very good conductor in the neighborhood of the critical point. The conductivity increases very largely for a saturated vapor as the critical point is approached owing to increasing density of both solvent and solute.

I take great pleasure in acknowledging my indebtedness to Professors Rising and O'Neil, of the Department of Chemistry, for a work room and for the facilities of their department. I wish, moreover, to acknowledge to the other members of the same department my appreciation of the many courtesies extended me.

PHYSICAL AND CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA,
BERKELEY, September, 1903.

SOME EXPERIMENTS ON THE POLARIZATION AND RECOVERY OF CADMIUM CELLS.

BY S. J. BARNETT.

ALL the elements used in these experiments were set up in small H-form vessels by me, following the methods of the Reichsanstalt with unimportant[1] deviations. The cells designated as Nos. 1, 2, and 3 were mounted about the middle of last November, and their e.m.f.s were first compared some ten days later. Their maximum difference was then about 1 part in 10,000, and in recent comparisons (except after severe treatment, described below) they have not differed by more than a few parts in 100,000. Nearly the same degree of excellence, tested either by agreement among themselves or by agreement with the cells of the first group, was attained within a few days after their mounting by Nos. 4, 5, and 6, which were set up on April 13, and Nos. 7, 8, and 9, which were set up on April 16. The mercury used in all the cells was from the same stock, while the other constituents were from different stocks for the cells of the first groups and those set up later. The paste in Nos. 4, 5, and 6 contained no free mercury. The volume of paste in No. 5 and in No. 6 was much greater than in any of the other cells (accounting for their high resistances).

The resistances of the cells were measured by a variety of methods, the only one wholly satisfactory being that of the bridge and secohmmeter with alternating currents. The resistances of Nos. 1, 2, 3, 4, 5, 6, 7, and 9, which will be denoted by $B_1, B_2, \cdots, B_9$, determined by this method on May 12 at 22°.3 C. were $B_1 = 361$, $B_2 = 401$, $B_3 = 342$, $B_4 = 408$, $B_5 = 571$, $B_6 = 587$, $B_7 = 351$, $B_9 = 421$, all in ohms. The resistance at the same temperature of No. 8, obtained by a different method but reduced to correspond with the above values by comparison with other cells whose resistances were determined by both methods, was about 435 ohms.

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[1] At least for the purposes of these experiments.

The temperature coefficient of the resistance of the cells at 20° C. was found to be -0.029. The resistances given above, properly corrected for temperature, were used in calculating the recovery curves given below.

The current through a cell during polarization was read on a Weston millivoltmeter of 5 ohms resistance.

The e.m.f.s of polarization during recovery experiments were determined by the differential method of direct deflections, which offered the advantages of great rapidity and sensitiveness. Two cells, one with normal e.m.f., the other polarized, were connected in series with a galvanometer and a box resistance of 100,000 ohms and the deflection read. The cells were then opposed to one another in the same circuit, the box resistance plugged out, and the deflection again read. If E_1 and E_2 denote the e.m.f.s of the two cells, B_1 and B_2 their resistances, G the resistance of the galvanometer, and $D+$ and $D-$ the deflections (corrected when necessary) with the cells in series and opposition respectively, the ratio of the difference of the e.m.f.s to their sum is

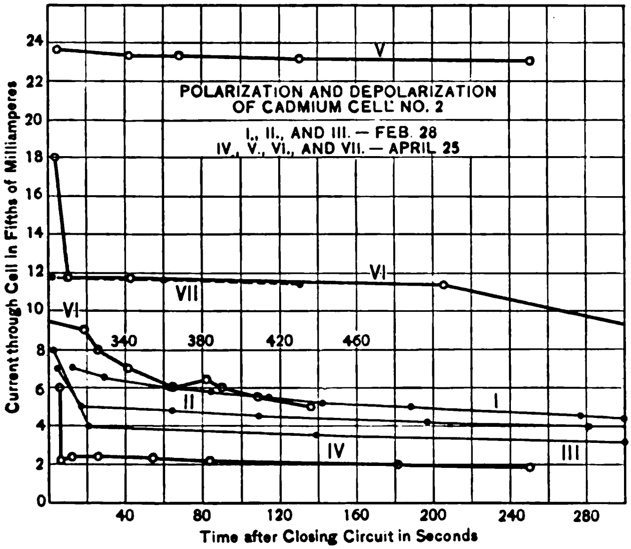

Fig. 1.

$$\frac{E_1 - E_2}{E_1 + E_2} = \frac{B_1 + B_2 + G}{B_1 + B_2 + G + 100{,}000} \times \frac{D-}{D+}$$

The method is open to the objection that during the recovery of the cell under test the standard cell is furnishing a current in such a direction as to polarize itself and to hasten the recovery of the other cell. Inasmuch, however, as the current was never greater than about $\frac{1}{1500}$ ampère at its maximum value in the early part of a recovery series, and fell in a few seconds to an excessively small value, the e.m.f of the standard cell was assumed to remain constant in calculating the recovery curves. The same method was used in comparing the e.m.f.s of the cells from time to time, although it must always give somewhat too close an agreement, and was occasionally roughly checked by a potentiometer. In some of the later experiments, in which the e.m.f. of polarization was very great, the box resistance was left in for both deflections.

The galvanometer was a heavy instrument of the Wiedemann type with a highly damped bell magnet, making it possible to begin observations about 6^s after closing the circuit. The variations of the null point were small and easily allowed for. The resistance of the coils used was about 500 ohms.

The time was recorded with a clock and chronograph or with a watch, according to the demands of speed and convenience. The temperature was read when necessary from a thermometer hanging on the wall.

After a few preliminary experiments more accurate observations began on February 28 with No. 1 as standard and No. 2 under test. No. 2 had been frequently short-circuited before, though never for a great length of time.

About $8^h\ 20^m$ $D+$ was 11.5 cm. and $D-$ was inappreciable (0.005 cm. could be detected, though readings were taken in general only to 0.01 cm.). At $8^h\ 22^m$ No. 2 was short-circuited through the millivoltmeter and its deflections and the time were read simultaneously for about five minutes. The observations are platted in Curve I. of Fig. 1.

At $8^h\ 27^m$ the circuit was broken and the cell connected for e.m.f. comparisons (through the galvanometer in opposition to No. 1). Simultaneous galvanometer and time readings were then taken for over ten minutes. From these data and the resistance $B_1 + B_2 + G = 1{,}375$ ohms, the recovery curve was calculated, and is platted as Curve I. of Fig. 2.

After a few resistance experiments the galvanometer was readjusted and $D+$ (= 38.1 cm.) and $D-$ (= 0.20 cm., $E_1 > E_2$ by 0.014 per cent.) were observed. At $9^h\ 32^m$ No. 2 was again short-circuited and a second polarization curve obtained, platted as Curve II., Fig. 1. After ten minutes the circuit was broken and a series of e.m.f. readings begun. The recovery curve calculated from these observations and from the resistance $B_1 + B_2 + G = 1{,}364$ ohms is platted as Curve II., Fig. 2.

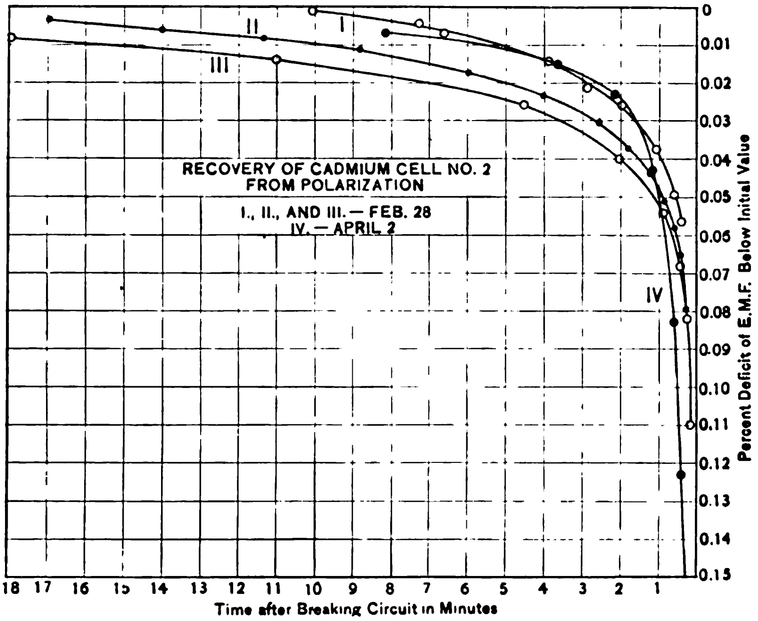

Fig. 2.

At $10^h\ 44^m$ the cell was again short-circuited, and at $10^h\ 31^m$ the circuit was broken and connections made for e.m.f. comparisons. The polarization observations are platted as Curve III., Fig. 1, and the earlier part of the recovery curve (calculated with $B_1 + B_2 + G = 1{,}353$ ohms) is platted as Curve III., Fig. 2. At $44^m\ 12^s$ after the circuit was broken E_2 differed from its initial value by less than 0.001 per cent. (The initial deflections before the polarization began were $D+ = 38.1$ cm. and $D- = 0.17$ cm., making $E_1 > E_2$ by 0.012 per cent.)

On April 2 several series of experiments were made upon No. 2. The apparatus was so arranged that all the combinations for the different measurements could be made by simply opening or closing keys, inserting plugs, etc.

At $9^h\ 36^m$ No. 2 was short-circuited for 3^m. At $10^h\ 2^m$ the process was repeated. At $10^h\ 39^m$ connections were made for e.m.f. comparisons. $D+$ was found to be 13.2 cm. and $D-$ to be 0.005 cm. ($E_2 > E_1$). At $10^h\ 45^m$ No. 2 was short-circuited through the voltmeter, whose reading fell to 1.7 millivolt at the end of three minutes, when the circuit was broken and the recovery observations began. The galvanometer deflection is platted as a function of the time after breaking the circuit in Curve II., Fig. 4 (the observations being indicated by the circular rings), and the recovery curve is platted in Curve I., Fig. 6. A part of the latter curve is also platted for purposes of comparison in Fig. 2 (Curve IV.). These curves were calculated with $B_1 + B_2 + G = 1{,}373$ ohms.

The low values to which E_2 fell after polarization in these experiments is evident from the polarization data and the fact that the initial current, calculated from the resistances and the initial e.m.f. of the cell, would exceed $1\frac{1}{6}$ milliampère.

To examine the (possible) variation of resistance during the time of recovery the following experiments were performed. An Edison cell (with e.m.f. 0.88 volt on April 3) was connected to the terminals of a resistance box with 1,010 ohms unplugged, and from traveling plugs connected with the terminals of the 10-ohm coil the current was led through the galvanometer, a reversing key, and the two cadmium cells in opposition. When the key was reversed the current was reversed through the cells, but not through the galvanometer. The deflection was read for both directions of the current through the cells, and the mean deflection at any time was taken as inversely proportional to the resistance $B_1 + B_2 + G$. The initial mean deflection was found to be 3.98 cm. No. 2 was then short-circuited for 3^m, at the end of which the circuit was broken and the cells connected as above with the current from the Edison shunt traversing No. 2 in the normal direction ($-$ to $+$). The galvanometer deflections were then observed as a function of the time after breaking the circuit. The results are platted in Curve I., Fig. 3.

After another short-circuit of 3^m, beginning at 12^h 3^m, a similar set of observations was made, but with the current traversing the cells in the opposite direction (+ to — in No. 2). The results are platted in Curve II., Fig. 3.

At 12^h 16–17^m deflections with the current in both directions through the cells were taken, the mean deflections in two sets being 4.00 cm. and 4.02 cm.

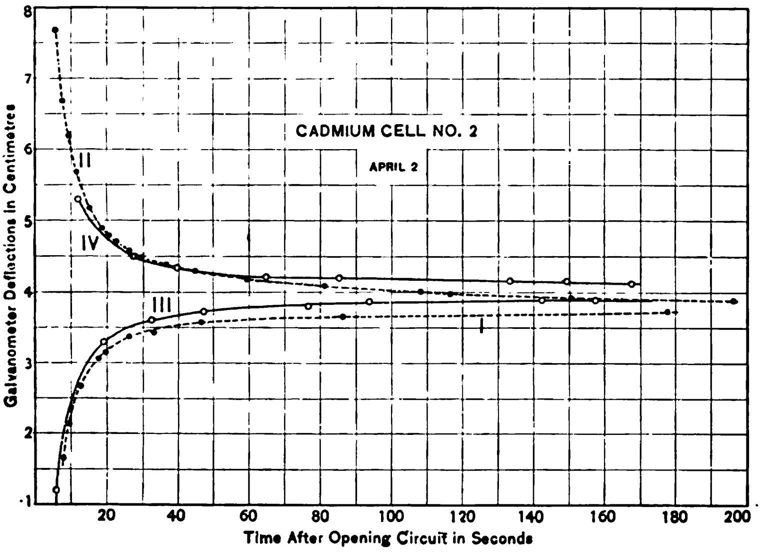

Fig. 3.

With the same connections, No. 2 was short-circuited for 3^m, put on open circuit for 1^m, short-circuited again for 1^m, then put on open circuit at 12^h 24^m with the current from the Edison shunt traversing it in the normal direction (— to +). The galvanometer deflection was read as soon as the oscillations of the needle had stopped, then the current was reversed through the cells and the deflection read, then reversed again, etc., times being read simultaneously with deflections. The results are platted in Curves III. and IV., Fig. 3; Curve III. containing the results with the current through No. 2 in the normal direction and Curve IV. the results with the current in the opposite direction.

The mean ordinate of Curves III. and IV., Fig. 3, is platted as a function of the time after open circuit in Curve I., Fig. 4, the first point, however, being obtained from Curves I. and II., Fig. 3.

The black circles on Curve II., Fig. 4, exhibit the relation between the half difference of the ordinates of Curves III. and IV., Fig. 3, and the time, the first point, however, being obtained from Curves I. and II of the same figure.

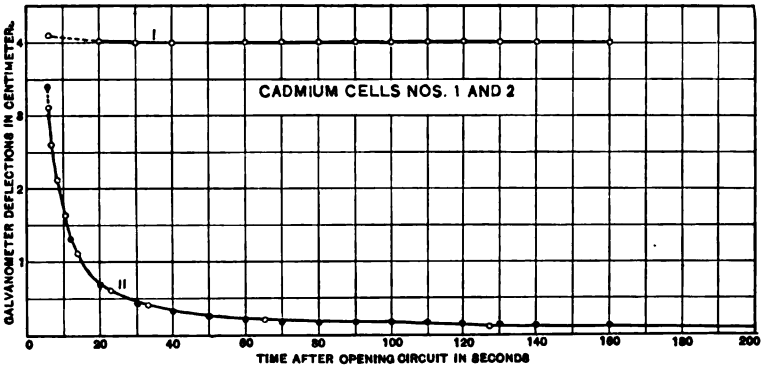

Fig. 4.

The figure (Fig. 4) shows that the resistance of the cells and galvanometer in series did not differ appreciably during the recovery observations from its initial value before short-circuit (deflection 4.01 cm.).

On April 22 observations were made upon cell No. 7, which had not previously been used (except from e.m.f. and resistance comparisons with extremely weak currents). Its initial electromotive force was found to be about 0.002 per cent. greater than that of No. 1.

At $10^h\ 62^m$ No. 7 was short-circuited and its polarization curve obtained. The observations are platted in Curve I., Fig. 5.

At $11^h\ 22^m$ the circuit was broken and recovery observations began. The results are platted in Fig. 6, Curve III., calculated with $B_1 + B_7 + G = 1{,}248$ ohms.

No. 7 was short-circuited again at $11^h\ 59^m$, and once more at $12^h\ 15^m$. The two sets of polarization observations are platted in Curves II. and III., Fig. 5.

The occurrence of maxima in some of the polarization curves is not peculiar to No. 7.[1] Such maxima have been observed with No.

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[1] Nor is it peculiar to cadmium cells. Nov. 14, 1903.

2 (as in Fig. 1, Curve IV.) and with No. 3, and would doubtless occur with any of the others if short-circuited sufficiently, unless perhaps the resistance of some of the cells is too great. In such cases maxima of the same kind could doubtless be produced by increasing the polarization current with the aid of an additional e.m.f., as in the case of Curve VI., Fig. 1 (see below).

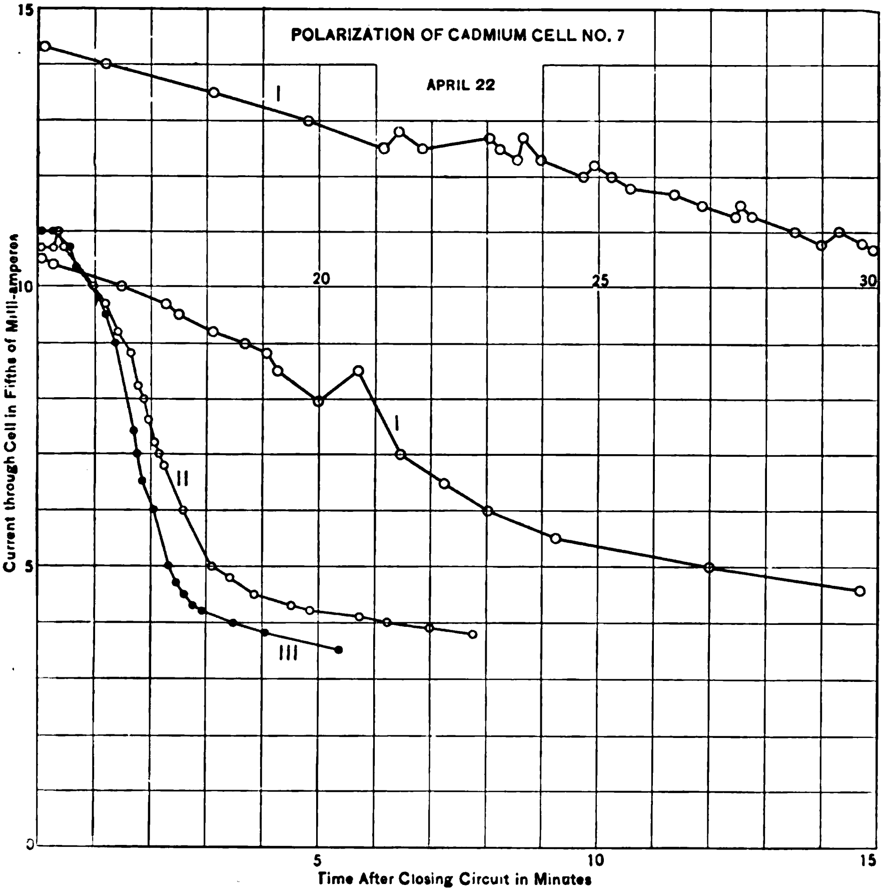

Fig. 5.

On April 25 cell No. 7, whose e.m.f. was then initially about 0.006 per cent. greater than that of No. 1, was short-circuited (without the voltmeter) at 8^h 41^m, and was so left until 12^h 52^m, when the circuit was broken. At 12^h 53^m the e.m.f. of No. 7 was only 9.7 per cent. of its normal value. Two days later its e.m.f. was less than that of No. 1 by only 0.001 per cent.

On April 25 some experiments were also performed upon Nos. 6 and 9, which had not been previously short-circuited. The initial differences between their e.m.f.s and that of No. 5, with which they were compared throughout the experiments, were 0.002 per cent. and 0.003 per cent.

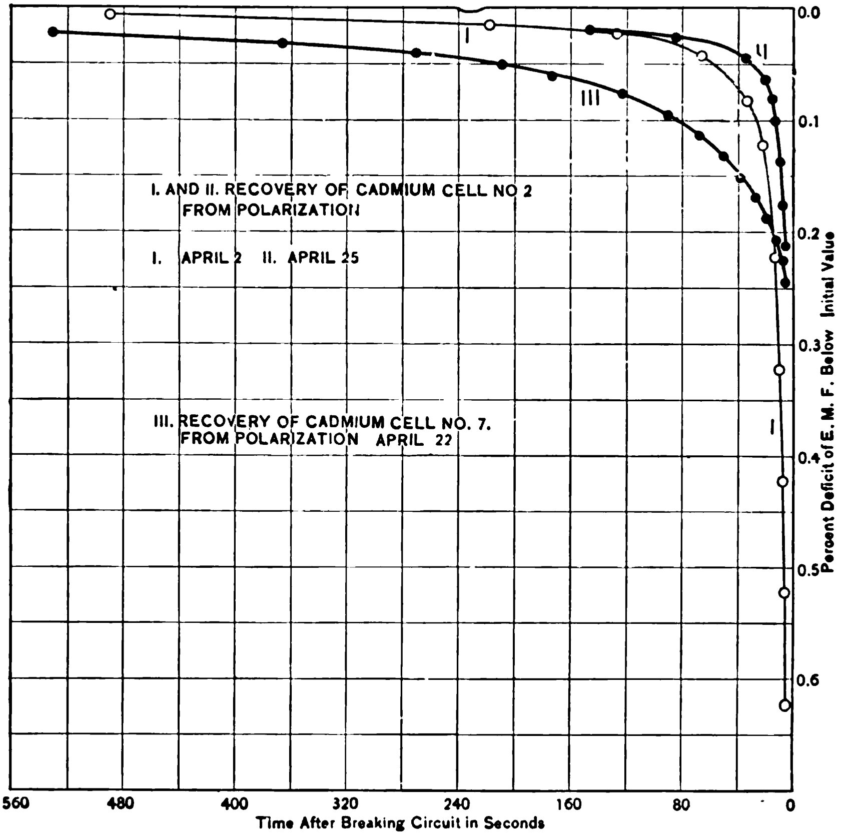

Fig. 6.

The polarization observations upon No. 9 are platted in Curve I., Fig. 7. Seven and one half minutes after the circuit was broken the e.m.f. had risen to within 0.02 per cent. of its initial value.

Cell No. 6 was short-circuited on the same day at 11^h 48^m and the circuit broken at 11^h 56^m. The polarization observations are platted in Curve II., Fig. 7. Four minutes after breaking the circuit the e.m.f. had recovered to within 0.03 per cent. of its initial value. At 12^h 0^m No. 6 was again short-circuited. The polarization observations are platted in Curve III., Fig. 7. In 16^m after opening the circuit the e.m.f. had risen to within 0.1 per cent. of its original value.

On the same day (April 25) some experiments were also made upon No. 2, whose e.m.f. was initially 0.0037 per cent. greater than that of No. 1. At 9^h 50^m No. 2 was short-circuited. The polarization observations are platted in Curve IV., Fig. 1. Although the cell had not been short-circuited since April 2, the curve shows all the peculiarities of an experienced cell.

About 4^m later the circuit was broken and recovery observations began. The results (calculated with $B_1 + B_2 + G = 1,378$ ohms) are platted in Curve II., Fig. 6.

A single chloride accumulator (e.m.f. = 2.03 volts) was then arranged to be connected through a key to the terminals of No. 2, with its positive pole to the negative pole of No. 2. The key was closed at 10^h 11^m and opened at 10^h 15^m 9^s. The observations are platted in Curve V., Fig. 1. After open circuit connections were made for e.m.f. comparisons (with 100,000 ohms in the circuit for both arrangements of the cells). At 10^h 22^m and 10^h 38^m the e.m.f. of No. 2 was 7.3 per cent. and 9.4 per cent., respectively, of its initial value.

The same accumulator was then closed in the opposite direction through No. 2 (at 10^h 40^m), and Curve VI., Fig. 1, was obtained. The circuit was broken at 10^h 48^m. Two minutes later the e.m.f. of No. 2, which had increased greatly after 200^s charging, was found to exceed that of No. 1 by only 0.1 per cent., which was reduced in 7^m more to 0.04 per cent.

In the first case (Curve V.) E_2 was reduced almost to zero, and in the second case (Curve VI.) it recovered its normal value within a few seconds. The resistance of the circuit did not alter greatly, if at all, at least in the earlier parts of the experiments.

The accumulator was then again connected to No. 2 (in opposition) and so left for 5^m. Two minutes after breaking the circuit (11^h 3^m 25^s) its e.m.f. was only 0.17 per cent. greater than that of No. 1. At 12^h 44^m the excess was only 0.02 per cent.

At 12^h 46^m No. 2 was short-circuited through the voltmeter. The observations are platted in Curve VII., Fig. 1, which resembles closely the polarization curve of a fresh cell. The approximate coincidence between this curve and a part of Curve VI. is due to the fact that the e.m.f. of the accumulator was almost exactly twice that of the cadmium cell. The e.m.f. of No. 2, on being tested just after breaking the circuit, was found to *exceed* that of No. 1 by 0.06 per cent. — a greater difference than before. Two days later the excess was 0.016 per cent.

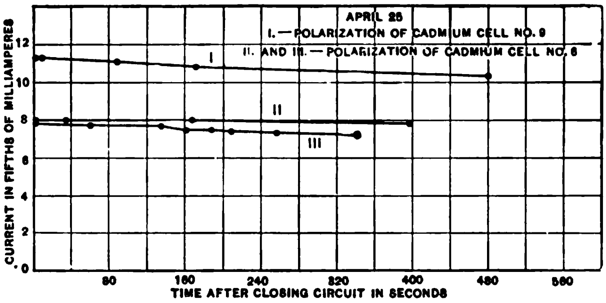

Fig. 7.

At 11^h 10^m two accumulators in series (e.m.f. = 4.1 volts) were connected to the terminals of Nos. 4 and 8 in opposition with the current in the normal direction through No. 8, and were so left until 12^h 26^m, when the circuit was broken. At 12^h 31^m the e.m.f. of No. 8 was only 6.9 per cent. of its original value, while that of No. 4 exceeded its initial value by 4.7 per cent. Two days later No. 8 had recovered to within about 0.006 per cent. of its normal e.m.f. and No. 4 to within about 0.09 per cent.

On May 2 at 12^h 52^m a dynamo with an e.m.f. of about 93 volts was connected in series with No. 4 and No. 8 in opposition, the current traversing No. 4 in the normal direction. Ten minutes later the cells had become considerably heated, and the upper part of the mercurous sulphate and adjacent liquid in No. 8 greatly perturbed. The circuit was then broken, and closed again a little later. At the end of about 2^m No. 8 exploded and broke the circuit. The e.m.f. of No. 4 was then tested and found to have fallen to 5.5 per cent. of its original value. On May 2 it had risen to 6.0 per cent., on May 7 to 9.4 per cent., and on May 12 to within about 0.27 per cent. of its initial value. Shortly after the last comparison the cell was charged for 1^m with a single accumulator (through the millivoltmeter). The e.m.f. was then found to exceed E_1 by 0.3 per cent., the excess rapidly diminishing to 0.15 per cent. On May 15, E_1 exceeded E_4 by 0.04 per cent.[1] (On May 12 the resistances of all the cells had been measured, both by alternating currents and by a charging current from 2 accumulators.)

Also on May 2, about $1^h\ 10^m$, the dynamo was connected in opposition to No. 7 and so left for about 30^s. The e.m.f., on being tested quickly after opening the circuit was found to exceed E_1 by 0.054 per cent., the excess decreasing to 0.04 per cent. by the next morning. On May 7 the e.m.f. of No. 7 was greater than that of No. 1 by 0.024 per cent. and on May 12 by 0.01 per cent. On May 15 the e.m.f. of No. 1 exceeded that of No. 7 by 0.001 per cent.

In most of the experiments here described I have been assisted by one of my students, Mr. C. K. Studley.

STANFORD UNIVERSITY, CALIFORNIA,
May 16, 1903.

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[1] In a comparison made yesterday E_1 exceeded E_4 by only about 0.004 per cent. Nov. 14, 1903.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE TWENTY-SECOND MEETING.

THE annual meeting of the Physical Society was held at the Central High School, St. Louis, Mo., on Wednesday, December 30, 1903, in coöperation with Section B of the American Association for the Advancement of Science.

Tellers being appointed by the President, the ballots for the annual election were counted and the following named officers were elected: President, Arthur G. Webster; Vice-President, Elihu Thomson; Secretary, Ernest Merritt; Treasurer, William Hallock; Members of the Council, E. Rutherford and W. S. Franklin.

The report of the treasurer for the year 1903 was read by the secretary. The report is printed below.

The following papers were presented:

1. The Radioactivity of Ordinary Metals. E. F. Burton.
2. Does the Radioactivity of Radium Depend upon the Concentration? E. Rutherford.
3. The Heating Effects of the Radium Emanation. E. Rutherford and H. T. Barnes.
4. The Phosphorescence of Organic Substances at Low Temperatures. Preliminary Note. E. L. Nichols and Ernest Merritt.
5. The Spectro-photometric Study of Fluorescence. E. L. Nichols and Ernest Merritt.
6. On the Electrical Conductivity of Liquid Films. Lyman J. Briggs.
7. On the Use of Nickel in the Core of the Marconi Magnetic Detector. Arthur L. Foley.
8. On Double Refraction in Matter Moving through the Ether. D. B. Brace.
9. Electric Double Refraction in Gases. D. B. Brace.
10. The Work of the National Bureau of Standards. E. B. Rosa.
11. The Spectrum of the Afterglow of the Spark Discharge in Nitrogen at Low Pressures. Percival Lewis.

12. The Spectrum of the Electrodeless Discharge in Nitrogen. PERCIVAL LEWIS.

On behalf of the Council the secretary made the following announcements:

Accepting an invitation from the Philosophical Society of Washington, the Council has decided to hold the spring meeting of the Physical Society in the year 1904 in Washington. The date of the meeting is to be decided by the officers of the Physical Society and will be announced later.

The Physical Society has been invited by the Committee of Organization of the International Electrical Congress to hold a meeting in St. Louis, in connection with the meeting of the Congress, during the month of September, 1904. The Council voted to accept this invitation, provided that mutually satisfactory arrangements could be made. It is the sense of the Council that a definite plan should be presented by the Council at this meeting for the establishment of a western section of the Physical Society.

ERNEST MERRITT,
Secretary.

Adjourned.

TREASURER'S REPORT FOR 1903.

Receipts.		
Balance from 1902	$1406.49	
Interest on the same to Dec. 31, 1903	49.23	
Arrears of dues for previous years	150.00	
Three life membership fees	150.00	
Annual dues	930.00	
Total		$2685.72
Disbursements.		
Printing, Andrus and Church	$ 102.40	
Subscriptions to Physical Review	591.00	
Subscriptions to Science Abstracts	295.50	
Office of the Secretary	112.34	
Office of the Treasurer	27.37	
Total		$1128.61
Balance carried forward		1557.11
Total		$2685.72

WILLIAM HALLOCK,
Treasurer.

DOES THE RADIOACTIVITY OF RADIUM DEPEND UPON ITS CONCENTRATION?[1]

BY E. RUTHERFORD.

BY the electric method, the intensity of the γ radiation from a known quantity of radium, in a state of radioactive equilibrium, was determined first in the form of pure solid radium bromide and second when dissolved in a solution of radium chloride of more than a thousand times the volume of the solid radium bromide. No appreciable difference in the intensity of the γ rays was observed in the two cases, although the experiments were continued over a month's interval. Since the intensity of the γ rays serves as a comparative measure of the radioactivity of radium, it may be concluded that, over the range examined, the radioactivity of radium is independent of its concentration. This result shows that the rate of disintegration of radium and its products is not appreciably altered by the bombardment of its own powerful radiations, and renders it probable that the radioactivity of radium is, in all cases, directly proportional to the amount of that element present.

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[1] Abstract of a paper presented at the meeting of the Physical Society held on December 30, 1903.

HEATING EFFECT OF THE RADIUM EMANATION.

BY E. RUTHERFORD AND H. T. BARNES.[1]

AN account of some preliminary experiments to show that the radium emanation, together with the secondary products which arise from it, was responsible for a large proportion of the heat emission of radium was given in *Nature* (October 29, 1903). Further results on this question were communicated to the Physical Society. The emanation from thirty milligrams of pure radium bromide was released by heat and condensed in a small glass tube immersed in liquid air. The variation with time of the heating effect of the deëmanated radium and of the tube containing the emanation was determined at regular intervals for over a month. A special form of differential air calorimeter was employed to measure the small heating effect involved. It was found that the heating effect of the emanation tube increased to a maximum after about three hours, and then decayed according to an exponential law with the time, falling to half value in a little less than four days. The heating effect of the deëmanated radium fell rapidly in the course of three hours to a minimum, corresponding to 25 per cent. of its original value and then slowly increased again with the time, recovering its original value after an interval of about one month. At any time during the whole course of the experiment the sum total of the heating effect of the deëmanated radium together with that of the emanation tube was constant and equal to that of the original radium. At any time t after reaching its maximum, the rate of heat emission Q_t of the emanation tube was given by $Q_t/Q_0 = e^{-\lambda t}$ where Q_0 is the maximum rate and $\lambda = .0077$ when an hour is taken as the unit of time. The rate of heat emission Q_t of the radium at any time t after reaching the minimum is given by $Q_t/Q_0 = .25 + .75(1 - e^{-\lambda t})$ where Q_0 is the maximum rate and λ the same constant as before.

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[1] Abstract of a paper presented at the meeting of the Physical Society held on December 30, 1903.

The variation of the heating effects with time, expressed by the above equations, is exactly the same as the variation of the radioactivity of the emanation and of the radium from which it has been separated, *measured by the α rays.*

The rapid initial changes of the rate of heat emission of radium after removal of the emanation and of the emanation tube after the introduction of the emanation were determined by means of a pair of differential platinum thermometers wound on the inside surface of a glass tube. By this method, observations could be made with more rapidity and certainty than by the air calorimeter. It was found that the heating effect of radium had fallen to about 59% of its original value 10 minutes after removal of the emanation. It then diminished steadily to a minimum of 25% after the lapse of 2 to 3 hours. After the heating effect of the emanation tube had risen to a maximum, the emanation was withdrawn and the diminution with time of the heating effect determined. There was a rapid drop during the first 10 minutes to about 45% of the maximum, then a slower change, and finally a more rapid decrease to zero according to an exponential law, falling to half-value in 30 minutes.

The curves showing the rise of the heating effect of the emanation to a maximum, and of the diminution of the heating effect of the emanation tube to zero after removal of the emanation, were found to be complementary to one another. The rapid fall and rise of the heating effect of the deëmanated radium and of the emanation tube respectively are connected with the fall and rise respectively of the "excited activity" produced by the emanation. It was suggested that the name emanation X be given to the matter which causes "excited activity" on bodies. On this view, the radium changes into the emanation and the emanation into emanation X. There are three further changes in the matter called emanation X. In the first change half the matter is transformed in 3 minutes, in the second change half in 34 minutes, in the third change half in 28 minutes. On account of the first rapid initial change in emanation X, it has not yet been found possible to separate the heating effect of the emanation from that due to the first change.

The results obtained are shown in the following table.

Active Products.	**Nature of Rays.**	**Percentage Proportion of Activity Measured by the α Rays.**		**Percentage Proportion of Total Heating Effect.**
Radium (freed from active products).	α rays.	25		25
Emanation.	α rays.	18	34	41
Emanation X (first change).	α rays.	16		
" (second change).	No α rays.	0	42	34
" (third change).	α β and γ rays.	42		

The results, as a whole show, that the heat emission of radium is an accompaniment of the expulsion of α particles and that the time-variation of the heating effect of each of the different active products is the same as the time-variation of the activity measured by the α rays. The heat emission of radium is probably due in part to the kinetic energy of the expelled α particles and in part to the energy released consequent upon the rearrangement of the components of the systems left behind after the expulsion of the α particle.

It was deduced that the emanation, released from 1 gram of radium, gave out an amount of heat during its life corresponding to about 10,000 gram calories. It has been shown (Rutherford, *Nature*, Aug. 20, 1903) that the volume of the emanation released from 1 gram of radium probably lies between 6×10^{-4} c.c. and 6×10^{-5} c.c. at standard pressure and temperature. Assuming the density of the emanation to be about 100 times that of hydrogen, 1 gram of the emanation would during its life radiate an amount of energy lying between 2×10^{9} and 2×10^{10} gram calories. One-pound weight of the emanation would initially radiate energy at the rate of 10^{4} to 10^{5} H. P. and would emit during its life an amount of energy between 6×10^{4} and 6×10^{5} horsepower-days.

There can thus be no doubt that matter, under special conditions, is capable of emitting an amount of energy enormous compared with that released in the most intense chemical reactions. On the disintegration hypothesis (Rutherford and Soddy, *Phil. Mag.*, May, 1903) this energy is derived from the energy latent in the radium atoms and is released during the successive stages of their disintegration.

THE PHOSPHORESCENCE OF ORGANIC SUBSTANCES AT LOW TEMPERATURES, PRELIMINARY NOTE.[1]

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

THE experiments here described are preliminary to a more extended study of phosphorescence and fluorescence at low temperatures, which will be, as far as possible, quantitative in character. Before undertaking quantitative experiments it seemed advisable, however, to test a large number of substances qualitatively, so as to determine which are best suited for further study.

The substances thus far tested are chiefly organic compounds of definite composition. Although a few had already been tried by Dewar, most of the substances had not been previously tested. Of the 120 substances tested only 21 failed to show either phosphorescence or fluorescence, or both, when cooled to the temperature of liquid air.

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[1] Abstract of apaper presented at the meeting of the Physical Society held on December 30, 1903.

The method of testing was briefly as follows: The substance was placed in a glass or porcelain dish in a dark room, and covered with liquid air, which was poured directly upon it. It was then illuminated by the light from a spark passing between magnesium terminals. Fluorescence. if at all intense, could be at once detected; while phosphorescence, if present, was observed after the spark had been stopped. By causing the light to pass through glass before reaching the specimen it was easy to determine whether the effects were caused by the ultra-violet or the visible rays. Each substance was also tested at ordinary temperatures. In the case of about one hundred substances the effect of X-rays was also tried, both at ordinary temperatures and when the substances were cooled by liquid air.

Previous experiments have shown that, as regards the effect of low temperatures on phosphorescence, bodies may be divided into at least three classes (1) substances in which the power to phosphoresce is increased by cooling; (2) substances which are phosphorescent at ordinary temperatures, but which have this power diminished or destroyed at low temperatures; (3) bodies whose behavior, as regards phosphorescence, is apparently unaffected by cold.

We have found many examples of the first class and some examples of the third; but among the organic substances studied no example of the second class was found. Balmain's paint and the phosphorescent sulphides are the only substances tested by us which show diminished phosphorescing power when cooled.

The effect of cold is manifested in a great variety of ways. Certain substances which show no luminescence at ordinary temperatures remain unaltered. Others, which are phosphorescent at ordinary temperatures, become more intensly so when cooled in liquid air. Phthalic acid and isophthalic acid are good illustrations of this class. Other substances, which are not luminescent at ordinary temperatures, become brilliantly so when cooled. Anthraquinone, ethyl carbamate, palmitic acid, and cetyl alcohol show intense phosphorescence at low temperatures, but none at all at 18°C. Certain substances, such as oxalic acid and piperine, develope the power of fluorescing at low temperatures. And, finally, there are many substances which become both phosphorescent and fluorescent when cooled in liquid air. Tetra-chlor-phthalic acid is a good example. This substance is also remarkable for the brilliant fluorescence produced, at low temperatures only, by the X-rays.

The X-rays seem much less effective in producing luminescence at low temperatures than light. In the case of tetra-chlor-phthalic acid the fluorescence is as brilliant as that of an ordinary X-ray screen. In several other cases also fairly intense phosphorescence or fluorescence is produced. But the greater number of the substances tested failed to respond.

In several instances there are indications that substances which are closely related chemically behave in a similar manner as regards their luminescence. The case of benzoic acid and calcium benzoate is perhaps the most striking. The various modifications of phthalic acid also show a general resemblance in their behavior. On the other hand, instances are far more numerous in which the chemical composition would lead us to expect similar behavior, while in reality none is observed. It has therefore been impossible, thus far, to develop any law connecting luminescence with chemical composition.

The Spectro-Photometric Study of Fluorescence.[1]

By E. L. Nichols and E. Merritt.

The law expressed by Stokes in his memoir entitled "Change of Refrangibility of Light," Philosophical Transactions, page 463, 1852, to the effect that in fluorescence the wave-length of the fluorescent spectrum is always greater than that of the exciting light has been called in question by Lommel[2] who pointed out that for certain fluorescent bodies there is an unmistakable overlapping of the regions in the spectrum occupied by the exciting waves and by the fluorescent light produced. Lommel drew the further conclusion that for this class of fluorescent substances the character and composition of fluorescence was independent of the wave-length of the exciting source. Lommel's exception to Stokes' law has found confirmation at the hands of Hagenbach, Stenger and others but his conclusions have been rejected and the universal accuracy of Stokes' law reaffirmed by Lamansky, Becquerel and others. It is the purpose of this paper to apply to the solution of this still open question the methods of the spectrophotometer. The authors have succeeded in getting data from which curves showing the distribution of intensities in the spectrum of fluorescene and of other substances, belonging to the same class can be plotted.

The most important conclusions reached in this paper are as follows:

(1) Not only in the case of these substances is Stokes' law inapplicable, but fluorescence can be excited by light, the wave-length of which is greater than that of the maximum of the fluorescent spectrum.

(2) Lommel's statement with reference to the independence of the fluorescent spectrum of this class of substances from the character of the exciting source is fully justified. The curves for fluorescence when excited by white light, by nearly monochromatic light of mean wave-length

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[1] Abstract of a paper presented at the meeting of the American Physical Society held on December 30, 1903.

[2] Lommel, Po[illegible]ndorff's Annalen, 14[illegible] and 160; also Wiedemann's Annalen, 8 and 30.

.5246, wave-length .494, and wave-length .465 gave curves identical as regards the position of the maximum, which in all cases was located at wave-length .517 μ. The shape of these curves is such as to indicate complete independence between the character of the exciting source and that of the fluorescence produced.

ELECTRICAL CONDUCTIVITY OF LIQUID FILMS.[1]

By L. J. Briggs and J. W. McLane.

REINOLD and Rücker[2] have found that the specific conductivity of a hard soap film increases as the thickness of the film decreases. In the case of Plateau's solution (*liquide glycerique*) no change in the specific conductivity of the film was observed down to a thickness of 374 $\mu\mu$. These conclusions are based upon the measurement of the thickness of the film by an optical method, which involves the assumption that the index of refraction of the film is the same as that of the solution in mass.

The writers have recently made some preliminary measurements of the specific electrical conductivity of films of Plateau's solution by another method, in which the thickness of the film is calculated from the surface area and *weight* of the film.

The measurements were made on a cylindrical film supported horizontally on two parallel platinum rings. The rings were soldered to two parallel vertical copper wires, which were held in a small ebonite frame. The film was enclosed during the measurements in a double-walled vessel, the walls of the inner vessel being kept moistened with the soap solution. The upper part of the frame passed through a slit in the cover of the vessel, and could be attached to the balance or to the bridge as desired.

Preliminary measurements by this method show that the specific electrical conductivity of a film approximately 1 μ in thickness is less than *one third* that of the solution in mass. The method involves the assumption that the density of the film is the same as that of the liquid in mass.

Bureau of Soils, Washington, D. C.,
December 24, 1903.

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[1] Abstract of a paper presented at the meeting of the Physical Society held on December 30, 1903.

[2] Phil. Trans., 1883, part 2, p. 645; 1893A, p. 505.

THE SPECTRUM OF THE ELECTRODELESS DISCHARGE IN NITROGEN.[1]

BY PERCIVAL LEWIS.

SOME general observations of the spectrum of the electrodeless discharge in various gases, and in gaseous mixtures showing an afterglow, have been made by J. J. Thomson[2] and by Newall,[3] but no systematic work seems to have been done on such spectra. The fact that in the ring discharge there is no passage of electricity between electrodes and the gas, no finite discontinuities nor even a potential gradient in the path of the current, and that the pressure in the gas is much less than that ordinarily employed in vacuum tubes, render it possible that some characteristic peculiarities may be observed in such spectra.

Nitrogen is a particularly interesting subject to study in this connection, as it has such a multiplicity of spectra, and several groups of bands which behave quite differently under given conditions. As it is often assumed that the negative-pole spectrum is due to cathode rays, it is also of interest to see whether the negative-pole bands appear in the spectrum of a discharge where there is no cathode.

The writer has recently obtained some preliminary results. The nitrogen was prepared by heating a solution of sodium nitrite and ammonium sulphate, mixed in molecular proportions. It was freed from traces of oxygen by bubbling through an alkaline solution of pyrogallic acid, and from carbon dioxide and water vapor by passing it through a concentrated solution of caustic potash and drying tubes.

The discharge tube was a spherical glass bulb, provided with a quartz window. Around it was a pasteboard cylinder on which were wound eight turns of heavy wire in circuit with a spark gap and condenser. The pasteboard cylinder was moistened to screen the tube from electrostatic effects, and the helix usually connected to earth. The ring was always very clearly defined, indicating that the electrostatic effects were at least very small.

At first the discharge was a coppery pink, characteristic of pure nitrogen. After a time it turned white, as likewise observed by J. J. Thomson, but the spectroscope showed without a doubt that the whiteness was due to mercury vapor from the pump, not to nitrogen, nor even to carbon compounds, the spectrum of which was vanishingly weak. Photographs were taken with a small quartz spectrograph, giving spectra of about 4 inches in length from λ 5,800 to λ 2,100.

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[1] Abstract of a paper presented to the Physical Society on December 30, 1903.

[2] Thomson, Phil. Mag., 32, 1892.

[3] Newall, Proc. Camb. Soc., 9, p. 295, 1897.

Deslandres[1] showed that in the spectrum of the positive column in nitrogen there are three distinct groups of bands, which are differently affected by physical conditions. The first group comprises most of the visible spectrum, and is attributed by Deslandes to pure nitrogen. The second begins in the violet and extends to about λ 2,800, and is supposed by him to be due to nitrogen and hydrogen. The third begins at about λ 3,000 and extends to λ 2,100. This group he considers dependent on the presence of traces of oxygen, as metallic sodium heated in the tube will eliminate it.

In the photographed spectrum of the ring discharge the third group is either entirely lacking, or with the longest exposures only faint traces of the strongest bands are visible. The second group of bands is strong. The first group is fairly strong. The difference between this spectrum and that of the simple induction discharge between electrodes is clearly shown by comparison with a plate showing the latter.

It is perhaps even more interesting to note that the negative bands also appear on all the plates, although weak in comparison with the positive bands. The only apparent way to reconcile this with the view that the negative bands are due solely to cathode rays seems to be to assume that there are electrostatic discharges from the glass walls, which thus act as electrodes. Some believe that the spectrum at the negative pole is due to the higher temperature at the cathode. It is very easy, however, to evoke the negative glow by merely placing the finger on the bulb, and no very high temperature seems possible with such a discharge. Whether or not the negative pole spectrum is due to cathode rays, it seems certain that it is not due to any temperature differences.

The stronger mercury lines, as well as some other lines not yet identified, appear on all the plates, as well as the strongest bands due to water vapor.

THE SPECTRUM OF THE AFTERGLOW OF THE SPARK DISCHARGE IN NITROGEN AT LOW PRESSURES.[2]

By Percival Lewis.

THE afterglow or phosphorescence often observed in vacuum tubes under certain conditions has been studied by many investigators.[3] In most of these cases, except that where pure oxygen is used (J. J. Thomson and Newall) the phosphorescence was observed in gaseous mixtures, it was produced by the simple induction or electrodeless discharge, and the spectrum was continuous — except possibly in one case where Thomson observed lines or bands with the ring discharge where nitrogen was used, and in the case of the afterglow arising from change of pressure in oxygen (Newall).

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[1] Deslandres, Ann. Chim. Phys. (6) 15, p. 46, 1888.

[2] Abstract of a paper presented to the Physical Society on December 30, 1903.

[3] See Kayser, Lehrbuch der Spectroscopie, Vol. 1, p. 249; Newall, Proc. Camb. Soc., 9, p. 295, 1897.

In 1899 the writer observed an afterglow which seemed different from those previously observed, both in origin and spectrum.[1] It was produced in nitrogen as pure as could be readily obtained, not in mixtures; it was produced only by a powerful discharge with spark gap and condenser, not at all by the simple induction or ring discharge; its visible spectrum was not continuous, but consisted of narrow bands or diffuse lines. The wave-lengths of these lines were difficult to determine accurately, but were about λ 6240, 5780, 5740 and 5410. The afterglow consisted of a rich chamois yellow fog, extending several inches into the connecting tubes. It persisted for several seconds after the discharge had ceased. It quivered and pulsated, and when fresh nitrogen was admitted the glow was driven as a luminous cloud before it, as in a similar case observed by Warburg.[2] It occurred through a wide range of pressures, ranging from a few millimeters to as high a pressure as would permit the passage of the discharge. The smallest perceptible traces of oxygen, hydrogen, carbon dioxide or water vapor completely destroyed it. If the nitrogen were previously passed over heated metallic sodium it did not appear. It seems possible that infinitesimal traces of oxygen may be necessary for its existence, while perceptible traces destroy it.

Recently the writer has discovered additional facts of some interest concerning this afterglow by photographing its spectrum with a quartz spectrograph.

The gas was prepared by heating a solution of sodium nitrite and ammonium sulphate, freed from traces of oxygen by passing through an alkaline solution of pyrogallic acid and dried by passing through a train of drying tubes.

As the phosphorescent glow extended some distance from the electrodes, it was possible to employ a device by which exposures could be made continuously while the discharge passed. A bent tube with a quartz window gave an end-on view of the afterglow, while the direct discharge was screened.

With aluminum electrodes the spectrum was found to be as follows: (1) The four lines in the visible spectrum previously noted, all strong and broad, not as yet identified; (2) the stronger heads of the positive bands of Deslandres' second and third group; (3) the stronger mercury lines; (4) four pairs of the strongest ultra-violet aluminum lines; (5) a number of unidentified lines.

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[1] Lewis, Ann. der Physik, 2, p. 459, 1900; also Astrophys. Jl., 1900.

[2] Warburg, Arch. des Sc. Phys. et. Nat., 12, p. 504, 1884.

On substituting platinum electrodes for the aluminum, the afterglow was unchanged in general appearance, and the visible spectrum and mercury lines remained the same. The aluminum lines were of course absent, while some new lines appeared — apparently not platinum. There were also some strong new bands in the ultra-violet, with heads toward the shorter wave-lengths, which have not yet been identified. The bands of the third group were as strong as when aluminum electrodes were used. Those of the first group were very weak.

The same spectrum was observed with iron electrodes, except that the second group of bands were a little stronger and some lines were absent.

We have in this afterglow apparently a kind of luminosity quite different from any other known in vacuum tubes. The state giving rise to it is due to the previous, not the coexistent discharge, and is far out of its path. The luminosity persists for many seconds after the exciting discharge, and gives not only the band spectrum of the gas, but the line spectrum of metals present in the tube, and other unknown lines.

The body of gas of which the spectrum was observed was at the nearest point about 15 mm. from the direct discharge and extended some four inches from it. Aluminum vapor must have existed in all this region. The phosphorescence followed the first discharge. It cannot, of course, be said with certainty that aluminum vapor took part in the initial phosphorescence — it may have been gradually torn off and diffused. But the remarkable and novel fact is that the aluminum vapor will radiate it all under such conditions. The aluminum lines are relatively the strongest in the spectrum of the afterglow; they are relatively very weak or absent in the spectrum of the direct discharge near the electrodes, where they might be expected to be strongest, if they occur at all.

The sensitiveness of this afterglow to impurities was strikingly shown by an accident. After putting platinum electrodes in the tube, attempts to secure the afterglow failed for several hours. It was finally discovered that there was a very slow leak due to a small crack near one electrode. The leakage was so slow that it made no perceptible difference in the 5-mm. pressure after more than an hour. On covering the crack with shellac the glow appeared immediately after introducing fresh nitrogen.

J. J. Thomson has advanced the hypothesis that afterglow effects are due either to chemical actions in a mixture, or to polymeric changes in a pure gas. If this be the explanation — and it seems a reasonable one — how can a chemically neutral gas excite luminosity in any metallic vapor which may be present, such as mercury and aluminum?

Some light may be thrown on this question by further investigations. Other questions which the writer proposes to attack are: Is the phosphorescence possible in absolutely pure nitrogen, or is the presence of any foreign substance necessary? If so, what foreign substance? How active a part do the metallic vapors play? What is the electrical condition of the phosphorescing gas? Do similar afterglows occur in other gases?

Mr. P. E. Rowell rendered efficient assistance in this investigation.

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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY
EDWARD L. NICHOLS
ERNEST MERRITT, and FREDERICK BEDELL

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MARCH, 1904

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THE

PHYSICAL REVIEW.

THE EFFECT OF THE INTENSITY UPON THE VELOCITY OF LIGHT.

By Thomas E. Doubt.

ANY measurement giving information upon that very important physical magnitude, the velocity of light, will aid the progress of physics. The relation between the intensity of light and its velocity of propagation is one of fundamental importance.

The most searching examination that has been made thus far into the effect of the intensity upon the velocity of light was that by Ebert.[1]

He tested for the effect of the intensity upon the velocity of light to one part in 860,000, where the intensity was varied in the ratio of one to twenty. Thallium light was employed as a source. In another experiment with light from a mercury spark (Hg α) the effect was tested for to one part in 840,000, where the intensity was varied in the ratio of one to two hundred fifty. He used many other sources of monochromatic light but in no case was the test carried to anything like the same degree of accuracy. His conclusion was "That the wave-length and therefore the velocity of propagation of light is to nearly a millionth part independent of its intensity when this is varied in the ratio of one to two hundred fifty."

The work of Ebert greatly exceeds in accuracy that of Lippich[2] or that of Muller.[3]

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[1] Wied. Ann., 1887, No. 32, p. 336.

[2] Wien. Ber., 1875, 272, p. 355.

[3] Pogg. Ann., 1872, p. 145.

Professor Michelson suggested that the effect of the intensity upon the velocity of light could be tested for with a much higher degree of accuracy by the aid of a form of interferometer such as was used in measuring the effect of the motion of the medium upon the velocity of light.[1]

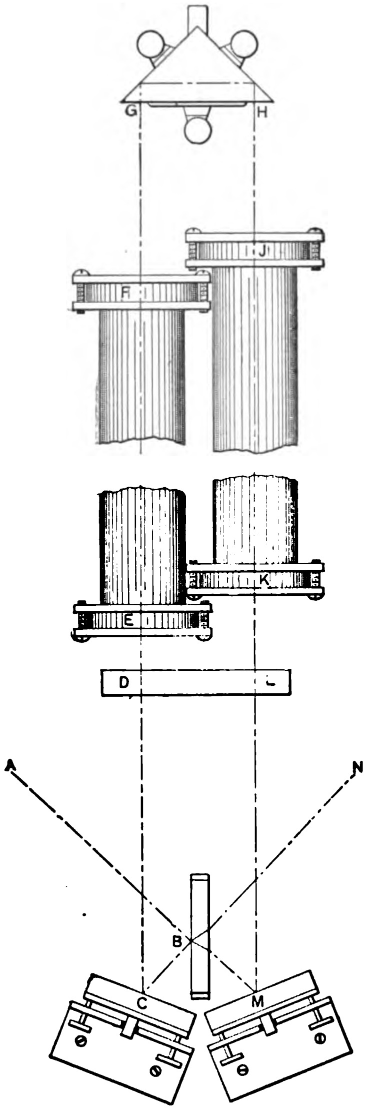

Fig. 1.

Description of Apparatus.

The form of apparatus used in this research is very similar to that used by Michelson and Morley in their investigation of the motion of the medium upon the velocity of light. Light from a source in the direction *A* (Fig. 1) meets the half-silvered surface *B* where it is separated into two portions. One part travels by the path *CDEFGHJKLMB* and the other by the path *MLKJHGFEDCB*. At the dividing glass *B* the two portions are reunited and are observed from the direction *N* by the eye or telescope. The reflecting surfaces *C* and *M* are plane glass silvered upon their front faces. *GH* is a large rectangular prism. *EF* and *KL* are brass tubes about 4.5 cm. in diameter with their ends closed with plane parallel glass plates. *DL* is a large plane parallel plate of glass silvered upon one surface in strips. One strip above is silvered so as to allow only one beam to pass through unhindered and similarly a strip below is silvered so as to allow the other beam free passage.

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[1] Am. Jour. Sc. (3), Vol. XXXI., 1886.

This silvered surface is used for reducing the intensity of one beam before it passes through the apparatus while the beam passing in the opposite direction is not reduced until it passes over the very large optical path. Numerous smaller plane parallel plates of glass silvered in strips were also introduced, usually only in one path at a time. Since the paths are identical it can make no difference with the center of the central fringe whether the plates are introduced at *D* or at *L*. In general, the introduction of a glass plate into the path of either beam will produce a change in the width of the fringes or a rotation of the fringes about some central point or both change and rotation.

The advantages of this arrangement are very marked. The apparatus permits the use of an extended source of light such as a gas flame, an arc light or sun light. Again it allows of a very large path over which the beams pass in different conditions and are then brought to the separating glass where they are made to interfere. One beam travels over a very large path with small intensity while the other travels over the same path with great intensity.

ADJUSTMENTS AND OBSERVATIONS.

The source of light was adjusted so as to give a beam meeting the dividing surface at an angle of 45°. All the surfaces were made approximately vertical. The rectangular prism was placed at a sufficient distance from the dividing surface upon a leveling table. The mirrors and prisms were respectively supported by brick piers. The mirrors at *C* and *M* were adjusted so as to give sharp vertical fringes. The plate *DL* was then placed in the path of the beam and both beams were allowed to pass through the clear portion and the plate was adjusted until the fringes were again vertical and sharp. The position of the central fringe was noted and the plate moved carefully so as to cause a silver strip to intercept one path. The position of the central fringe was noted.

This procedure was carried out first with air between the rectangular prism and the mirrors, the distance between them being about 220 cm. For very dense silver films the selective absorption was noticeable but with films of medium density the effect was much the same as if a light cloud had come over the sun, the intensity only being cut down and the colors changed but little. This effect of selective absorption is more noticeable when determining the amount of transmitted light by means of the photometer. The total optical path over which the two beams pass in different conditions is 460 cm. This was calculated by taking into account the distance in glass and its refractive index as well as the distance in air. If the mean wave-length is taken as .000057 cm. the optical path is over eight million wave-lengths. If it is assumed that a shifting of one thirtieth of the width of a fringe may be readily detected then a change in velocity of one in 240 million could be detected or a change of 240 cm. per sec.

In estimating the sensitiveness of the method a series of settings of the eye-piece micrometer of the observing telescope was made on the dark fringes bordering on the central fringe. The intersection of the diagonal cross wires (Fig. 2) was used to determine the location of the fringes. This figure represents the field of view of the telescope with two vertical wires attached to the micrometer removed so as to represent the fringes more clearly. The fringes were usually so adjusted that there were seven in the field of view.

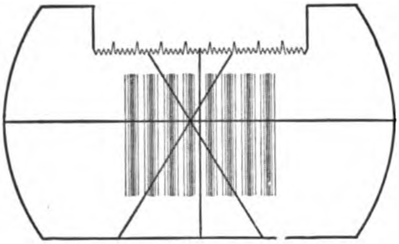

Fig. 2.

The following results were obtained with white light:

Reading of micrometer head with three turns between each setting increasing from left to right.

		Width of Central Fringe.	Difference from Mean.
Left.	74.4	377.2	−19.1
Right.	52.6	392.6	− 3.7
Left.	60.0	394.6	− 1.7
Right.	54.6	399.0	2.7
Left.	64.4	408.6	12.3
Right.	63.2	402.5	6.2
Left.	60.3	400.7	3.4
Right.	61.4		
		Mean 396.3	Variation 7.01

The sum of the differences is 589.52. The mean error of one observation is 9.81 or 2.5 per cent. The probable error of the result is 1.18 or .29 per cent. One would seem justified in concluding from the above results that if a shifting of a hundredth of the width of a fringe took place it could be detected. In what follows I have assumed that a shifting of one thirtieth of a fringe could be detected with certainty.

A large number of silver films were used of increasing opacity until one was found through which the light could barely produce visible interference fringes. The amount of light transmitted by the silver film was measured by Glan's Photometer. The film allowed one part in 290,000 to pass through. Thus one beam travels over a path of 460 cm. with an intensity only one part in 290,000 of that of the other beam and if a change in velocity of 124 cm. per sec. occurred it could be detected. No shifting of the central fringe was observed.

The tubes were now introduced and the experiment repeated. The tubes contained air. No new facts develop. The fringes were somewhat steadier with the tubes in the path than without them. When the tubes are filled with distilled water the optical path is greater than with air. The tubes in one case were each 200 cm. in length. The optical path amounted to 593.4 cm. or 10,400,000 wave-lengths in air. If a change in intensity produced a change in velocity of 100 cm. per sec. it could be detected.

The results of the two sets of experiments may be tabulated in the following manner:

Ratio of Intensities.		Length of Optical Path.	Change of Velocity that Might be Detected.
Air	1:290000	460 cm.	124 cm. per sec.
Air	1:290000	1000 "	57 " " "
Water	1:250000	593 "	100 " " "
Water	1:43000	1289 "	42 " " "
Carbon disulphide	1:43000	707 "	80 " " "

The experiment was tried by adjusting the fringes so that they made an angle with the vertical. The silver film was inserted and the position of the central fringe was noted. No displacement was noted at angles of about 45° or 135° or when the fringes were horizontal. Hence it may be concluded that change of azimuth has no effect.

These experimental results for light traveling in air justify the conclusion that a change in intensity of one in 290,000 does not change its velocity by 57 cm. per sec. In the case of water a change in intensity of one in 43,000 does not produce a change of 42 cm. per sec. In the case of carbon disulphide the same change in intensity does not produce a change in velocity of 80 cm. per sec. It seems very probable from the settings taken with the eyepiece micrometer that a shifting of one fiftieth of the width of a fringe could be detected. Hence a change in intensity from 1 to 40,000 in water does not affect the velocity to one part in 1000 million.

Grateful acknowledgments are due Professor Michelson for his helpful suggestions. Much assistance has been received from Dr. Mann and the staff of Ryerson Physical Laboratory.

University of Chicago,
May 4, 1903.

ON THE NATURE OF CERTAIN RADIATIONS FROM THE SULPHATE OF QUININE.

By Fanny Cook Gates.

IN studying the properties of certain substances known to become phosphorescent by a change in temperature, G. Le Bon found that when the sulphate of quinine is either heated or cooled through a high range of temperature, it becomes temporarily phosphorescent and possesses the power of discharging the leaves of an electroscope. He believed this effect to be due to chemical reaction, dehydration taking place when the quinine is heated above 100° C. and hydration upon cooling it again, and from this he argued that the radiations from radium and the other active minerals may be due to slight internal temperature changes and entirely explained by chemical reactions.

The ionization of the gas is the accompaniment of so many phenomena of totally different origin and character that before such a theory as M. Le Bon advances can be tenable to any degree, it must be proved that the radiations he describes possess other properties characteristic of those from the naturally radio-active substances, in addition to the property of causing the surrounding air to become a conductor of electricity. The experiments described in the following pages were undertaken for the purpose of determining the exact nature of the radiations emitted by the quinine sulphate under the conditions named, and of ascertaining to what extent they are similar to those given off from the radio-active substances.

The first tests were made with one gram of quinine sifted uniformly over a metal plate 20 cm. square. This was heated over a spirit lamp and then allowed to cool to the temperature of the room between parallel metal plates within a closed vessel. The plates were about 5 cm. apart and insulated. The lower one on which the quinine rested was joined to one terminal of a storage battery of 300 volts and the upper one to the electrometer, other connections being made in the usual manner. The strength of the current passing between the plates as indicated by the deflection of the electrometer was used as a measure of the rate of radiation from the quinine.

With the apparatus arranged as above described, it was found that after removing the quinine from the source of heat no deflection of the electrometer was at first produced, but that after about two minutes a slight current was noticed which increased slowly at first and then rose suddenly to a maximum at the end of about five minutes. It then rapidly decreased and the effect apparently ceased altogether after fifteen minutes. This variation of the radiation with time is shown in Fig. 1. On account of the rapid rate of change in current while passing through its maximum value, it was impossible to make accurate determinations near that point and the curve gives its value only approximately.

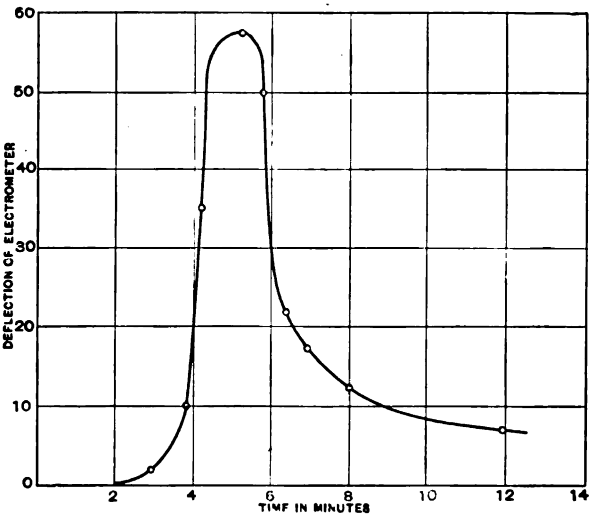

Fig. 1.

Upon reheating the same quinine and observing under apparently similar conditions, it was found that although curves of the same general type were obtained, the total radiation produced during successive tests varied greatly. This seemed to indicate either that repeated heatings of the quinine changed its power to emit rays or that slight differences in the temperature to which it was heated produced comparatively large changes in the resulting radiation. For this reason the spirit lamp was discarded and the quinine was heated to a definite temperature in a hot air bath. When allowed to cool from this temperature successive tests of the same substance gave curves of the same magnitude showing that the treatment had caused no inherent change in the quinine and that a slight variation in the temperature range produced a definite change in the resulting radiation.

RANGE AND RATE OF COOLING.

By the range of cooling, is meant the total number of degrees through which the quinine is cooled during a single test. The rate of cooling is the fall in temperature per second.

As has been stated, the ionization of the surrounding air is produced during the process of heating as well as that of cooling the quinine, but the experimental difficulties in obtaining accurate measurements of the radiation were so much greater in the former process than in the latter, that we have here confined our attention to the results obtained during cooling.

Two series of tests were made in which the temperature range was made to vary. In the first set the upper temperature was changed for each test while the lower one was kept always the same. In the second set the upper temperature was kept constant, and the effect noted by cooling the quinine from this temperature to different lower ones. This was accomplished by placing the parallel plates, between which the ionization took place, inside an air-bath the temperature of which could be regulated. These observations made it possible not only to test the effect of increasing the range and the rate of cooling, but to compare the effects produced by equal falls in different parts of the scale, and thus to determine where the maximum radiation is produced.

From the first set of observations, about 180° C. was found to be the highest temperature to which the quinine could be heated without permanent chemical change, and no appreciable radiation was observed unless the quinine was heated above 70° C. A comparison of the currents observed at the end of four different temperature ranges, each having the same lower limit is given in the following table. The current is here measured in an arbitrary unit of the order of 10^{-13} amperes and in each case the current at the end of five minutes after heating is approximately the maximum current for that test.

Upper Temperature.	Lower Temperature.	Range.	Current After 5 Minutes.	Current After 10 Minutes.
180° C.	18° C.	162°	75	20
165	18	147	50	16
100	18	82	20	11
75	18	57	10	7.5

From the second series of experiments due to changing the lower temperature of each cooling, a normal fall from 180° C. to 50° C. was found to produce but little effect, but when the lower limit was below 40° an increase in the range produced a rapid increase in the current. The total quantity of electricity discharged by the rays however did not increase when the lower temperature was below 18° or 20°. Thereafter an increased rate of radiation due to an increased rate of cooling was counterbalanced by a decrease in the

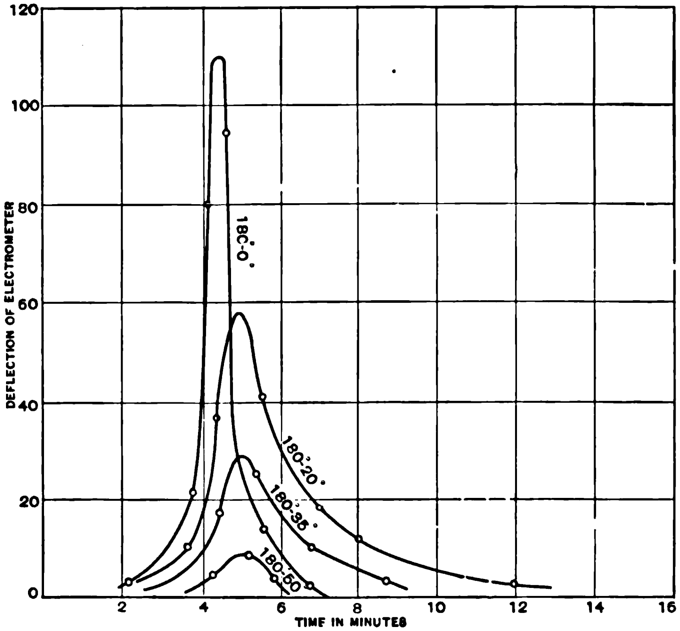

Fig. 2.

time during which the radiation continued. The curves shown in Fig. 2 illustrate this. When cooled to 0°, the maximum current was nearly twice as great as when cooled to 20°, but the effect lasted only half as long. A similar but more marked effect was observed when the testing plates were placed over a vessel containing liquid air. In this case the current rose almost immediately to a high maximum value, but the effect apparently ceased within three minutes. Thus it would seem that *the total radiation is not increased by an increase in range when the lower limit is below 20°.*

The fact that an increase in the range from 180° to a point below

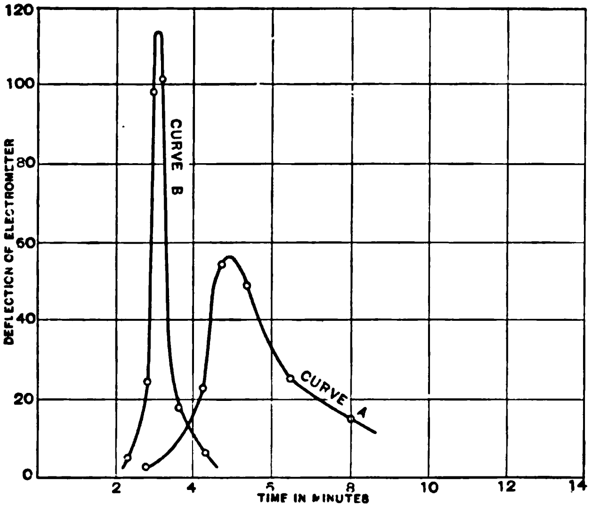

Fig. 3.

20° increased the rate of radiation at the expense of the time it continued would be entirely explained by the increased rate of cooling, providing the rate of radiation is solely determined by the rate of cooling during a given change. Direct experiments were therefore made in which the cooling was hastened by blowing dry dust-free air between the parallel electrodes as soon as the quinine was in place. In Fig. 3, Curve A shows the rate of radiation under normal cooling, while B is the curve when the cooling was hastened in the manner described, the range being the same. The similarity of the latter curve with that in Fig. 2 caused by the 180°–0°

range is striking and strongly indicates that *an increase in the rate of cooling increases the rate of radiation but does not change the total radiation during a single cooling.*

Consistent with these results were those obtained by using very thin layers of quinine. One fifth of a gram scattered over a given area was found to give as large a maximum current as that derived from one gram over the same space, but the radiation continued for a correspondingly shorter time. This is entirely explained by the more rapid cooling of the thin than of the thick layer. When heated on a thick metal plate the effect was less than when a thin plate was used, presumably because it retained the heat and retarded the cooling. Plates of different metals of uniform thickness gave no appreciable difference in the radiation. Similar but more marked results were obtained by saturating the air of the testing vessel with water-vapor, and also by spraying the quinine itself with water. In both cases the decay of the radiation was hastened.

The above results were all obtained with an air space between electrodes of about two inches and a potential difference of 300 volts. By attaching the upper plate to an insulated screw of known pitch it was possible to vary the distance between the plates as much as desired. Before this question of the absorption in air could be satisfactorily investigated it was necessary to determine the effect produced by increasing the P.D. between the electrodes.

EFFECT OF VOLTAGE. SATURATION CURVE.

One of the chief characteristics of the radiations from the active elements is that after a certain strength of electric field is attained a further increase in the potential difference will not increase the

Voltage.	**Current After 10 Minutes.**				
	First Test.	**Second.**	**Third.**	**Average.**	**Ratio.**
900	32.0	33.5	32.8	32.8	100
600	23.5	23.9	24.0	23.8	72
300	13.0	13.7	13.4	13.4	41
Voltage.	**Current After 5 Minutes.**				
900	21.5	21.5	23.5	22.2	100
600	15.5	15.7	17.0	16.1	72
300	8.5	9.2	9.5	9.1	41

ionization current; that is, a saturation current is obtained which cannot be increased with voltage.

The effect of voltage on the radiations from quinine sulphate was found to be very different, as will be seen from the tabulated results obtained from three coolings of the same quinine, during which the potential difference was each time varied. These results on a current voltage diagram (Fig. 4) give no indication of a saturation value to the current, although the strength of the field is about twenty times as great as that sufficient to produce saturation for radium radiations under similar conditions.

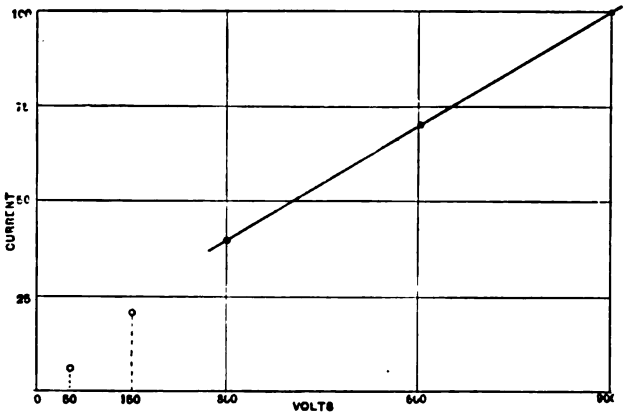

Fig. 4.

Observations were made with various widths of air space, but although the plates were brought to within 2 mm. of each other, no indication of saturation was obtained for a P.D. as great as 900 volts. An attempt was also made to determine whether with low voltages, the current might not vary as the square of the P.D. but no definite results could be obtained. With 150 and 50 volts respectively the values found for the current when expressed in ratio as above were 21 and 5 (see Fig. 4).

ABSORPTION BY AIR AND OTHER SUBSTANCES.

Since no saturation current could be obtained it was impossible to secure a value of the coefficient of absorption in air, but by varying the width of the air space and keeping a constant potential difference between the plates, results were obtained which were a marked contrast to those produced with the uranium, thorium and radium radiations.

As has already been stated all observable effect from the quinine ceased within fifteen minutes of the time of heating when the distance between the plates was 5 cm. When the width of the air space was reduced to one half of this value the value of the maximum current was approximately doubled, and the electrometer deflection was easily observed for thirty or forty minutes. When the electrodes were only 3 mm. apart the effect was clearly observed for over two hours. The actual numerical values obtained from observations with a P.D. of 900 volts are shown in the following table:

Distance in Centimeters Between Electrodes.	Current After 10 Minutes.	Current After 20 Minutes.
5.0	1.6	1.0
2.5	7.4	4.5
1.2	14.0	10.5
.3	32.0	20.0

With the electrodes 3 mm. apart and with a potential difference of 900 volts between them, a sheet of aluminum foil only .003 mm. thick was found to cut out all effect and the radiations were also found to be unable to penetrate a thin sheet of paper. This offers perhaps the most striking contrast between the two types of radiations since the most easily absorbed rays from radio-active substances will penetrate several layers of aluminum foil with comparatively little loss in intensity.

Both quartz and glass plates 2 mm. thick were placed over the quinine in turn and although no deflection of the electrometer was produced these results can carry no evidence one way or the other since the conditions prevented a sufficiently rapid rate of cooling.

DIRECTION OF THE ELECTRIC FIELD.

One of the most unexpected and suggestive phenomena connected with the radiations under discussion is that caused by changing the direction of the electric field. When the plate on which the quinine rested was joined to the positive pole of the battery, the resulting ionization was invariably greater than when joined to the negative pole. This effect was more marked when the plates were far apart, but even when the space between the electrodes was only 3 mm., the ratio of the current obtained by joining the lower plate to the positive pole of a 600-volt battery to that obtained by joining it to the negative pole was 1.2. This ratio for other distances is shown in the following table:

Distances in Centimeters Between Electrodes.	Ratio.
.3	1.20
1.2	1.48
2.5	1.64
3.7	1.93
7.5	2.53

This marked effect indicates that the radiations may possibly be produced by ultra-violet light. The current voltage curves are very similar to those obtained when ultra-violet light falls on a charged surface, except that here both positive and negative ions are present. The difficulty in obtaining saturation may be due to the fact that the ionization takes place very close to the surface of the quinine and the ions consequently rapidly diffuse to its surface and cannot be removed without a very intense field. The difference in the positive and negative currents is probably due to a difference in the size of the positive and negative ions, the positive ions traveling faster than the negative ones. A difference in their size could be explained by the condensation of vapor around them in the same way as the ions in flame gases increase in size when the gases cool. The whole effect appears to be due to some type of radiation which is easily absorbed in the gas and since the electrical effects are accompanied by marked phosphorescence it seems possible to suppose that the ionization may be caused by very short waves of ultra-violet light such as Lenard has shown to be active in ionizing the gas.

Optical Effect.

Mention has been made of the phosphorescence accompanying this phenomenon. The quinine when heated in a dark room was observed to glow for about fifteen minutes while cooling. The light given off was bluish white in color but was of insufficient intensity to admit of optical measurement.

SUMMARY.

In conclusion let us contrast those properties found to be most characteristic of the quinine radiations with those obtained under similiar conditions from radio-active bodies.

1. The quinine radiations are only apparent when accompanied by a great temperature change. The rate of ionization varies during this change and in a short time the effect ceases altogether. The rate of discharge of electricity between plates exposed to the radiations from the active elements, however, is incapable of alteration by any change in temperature, and so far as is known these radiations suffer no alteration with time.

2. By increasing the strength of the electric field it is impossible to secure a maximum ionization current from quinine radiations while a comparatively weak electric field is sufficient to produce a saturation current due to the radiations from radium and the other active elements.

3. The quinine radiations are certainly largely absorbed by at least two or three mm. of air and may be absorbed by a much shorter distance, while the least penetrating radiations from the active elements will pass through several cm. of air without great loss in intensity.

4. The quinine radiations are completely absorbed by a very thin sheet of aluminum which does not cut out the rays of uranium, radium and thorium.

5. The rate of ionization due to radium radiations is independent of the direction of the field, whereas that from quinine radiations undergoes a marked change upon reversing the direction of the field.

These conclusions show very clearly that there is no evidence for believing that the ionization from quinine radiations is due to the spontaneous projection of charged masses from the atom as in the case of radio-active bodies, but to molecular actions which are influenced by temperature.

While M. Le Bon is therefore undoubtedly correct in his assertion as to the nature of the cause of the quinine radiations, these experiments show no justification whatever for attributing the radiations from radium and the other active bodies to a similar cause, but on the contrary testify to a fundamental difference in production.

I desire to express my deep obligation to Professor Rutherford for his kind interest and direction during the course of these experiments.

MACDONALD PHYSICS BUILDING,
McGILL UNIVERSITY, June, 1903.

A STUDY OF THE MOLECULAR LOWERING OF THE FREEZING-POINT OF WATER PRODUCED BY CONCENTRATED SOLUTIONS OF ELECTROLYTES.

By Harry C. Jones and Frederick H. Getman.

Historical Review.

IN applying the freezing-point method to the then newly discovered theory of electrolytic dissociation Arrhenius[1] noted that the molecular depressions for solutions of calcium, strontium and magnesium chlorides, and cadmium iodide decrease with increasing concentration to a certain minimum value and then increase again.

Arrhenius[2] found that solutions of cane-sugar, dextrose, mannite and glycerine also exhibit this same phenomenon. Raoult[3] observed this abnormality in his studies on the freezing-point depressions of calcium nitrate, magnesium sulphate and copper sulphate.

Other workers in this field have made the same observations. Among these may be mentioned Loomis,[4] Barnes,[5] Jones,[6] Jones and Ota,[7] Jones and Knight[8] and Ponsot.[9]

The first systematic study of this phenomenon, however, was made by Jones and Chambers[10] in 1900.

They determined the molecular depressions for solutions of calcium, barium, strontium, magnesium and cadmium chlorides and bromides, the concentrations varying from $\frac{1}{500}$ normal to normal.

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[1] Ztschr. phys. Chem., 2, 496.

[2] Ibid., 2, 495.

[3] Ibid., 2, 488.

[4] Wied. Ann., 57, 503.

[5] Trans. Roy. Soc. of Canada, Vol. VI., Sec. III., 37.

[6] Ztschr. phys. Chem., 12, 642.

[7] Amer. Chem. Jour., 22, 5, 1899.

[8] Ibid., 22, 110, 1899.

[9] Recherches sur les congélations, Paris, 1896.

[10] Amer. Chem. Journ., 23, 89, 1900.

With all the salts, except cadmium chloride and bromide, minima were found. In addition to determining the molecular depressions for these solutions the authors also measured the conductivities in order to see whether there existed any irregularity in the conductivity curves in the same region of concentration where the abnormal depressions became manifest. To quote their own words: "An examination of the conductivity curves shows no irregularity in the region where the molecular lowering of the freezing-point becomes a minimum. The conductivity curves are just such as would be expected for any strongly dissociated electrolyte in water. The conductivity increases regularly from the most concentrated to the most dilute solution investigated, and shows a continually increasing dissociation with increase in dilution."

The work of Jones and Chambers was extended by Chambers and Frazer,[1] who studied hydrochloric and phosphoric acids, sodium acetate, copper sulphate, zinc chloride, strontium and cadmium iodides. In each one of these cases a more or less well defined minimum was observed. In 1902 W. Biltz[2] published the results of his further extension of the work inaugurated by Jones and Chambers. He, together with Julius Meyer, studied the following substances: Cassium chloride, rubidium chloride, potassium chloride, ammonium chloride, sodium chloride, lithium chloride, mercuric chloride, cupric chloride, zinc chloride, manganous chloride, nickel chloride, cobalt chloride, ferrous chloride, aluminium bromide, cupric bromide, potassium sulphocyanate, potassium cyanide, potassium bromide, potassium iodide, potassium fluoride, lithium nitrate, lithium bromide and lithium iodide.

The concentrations varied from $\frac{5}{100}$ normal to $\frac{3}{2}$ normal. In almost every case well marked minima in the molecular lowerings were observed, the following salts being exceptions; rubidium chloride, potassium chloride, lithium chloride, aluminium bromide, potassium sulphocyanate, potassium cyanide, potassium bromide and lithium iodide.

In all of these investigations the observations were confined to comparatively dilute solutions; in no case did the concentrations have a wider range than from extreme dilution to $\frac{3}{2}$ normal. It seemed very desirable to extend this work to solutions of greater concentration and, to study in this way a large number of different substances.

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[1] Am. Chem. Jour., 23, 512, 1900.

[2] Ztschr. phys. Chem., 40, 185.

OBJECT OF THIS INVESTIGATION.

The object of this investigation as already stated, is to extend the work in this field by studying solutions of greater concentration, especially by means of the freezing-point and conductivity methods. By applying these methods to a large number of substances differing widely in chemical and physical properties, it seemed probable that some light might be thrown upon the problems presented by concentrated solutions, and that through such studies we may come to understand why the laws which obtain for dilute solutions fail completely when applied to solutions of greater concentration.

APPARATUS.

Freezing-Point Apparatus.

The accompanying figure (1) shows the apparatus used in determining the freezing-points of the solutions. It will be seen to be essentially that devised by Beckmann. The thermometers used were made expressly for this work. They were of the Beckman type, one having a range of *twelve degrees*, each degree being divided into fiftieths, the other having a range of *twenty-five degrees*, each degree being divided into twentieths. The thermometer with the greater range was employed when working with very concentrated solutions, which gave a large depression, while the more finely divided instrument was used with the more dilute solutions.

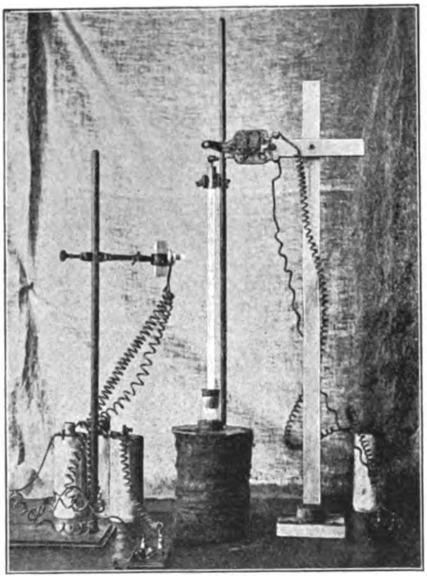

Fig. 1.

The stirrer in the freezing tube consisted of a ring of stout platinum wire around which was wrapped a spiral of fine platinum wire. The size of the ring was such that when wrapped with the smaller wire it would just touch the walls of the freezing tube and thus hinder the formation of an ice-sheath. This device was found to give perfect satisfaction, and to be in every sense superior to the ordinary glass stirrer. The platinum stirrer was attached to a glass rod which passed closely through a glass tube in the cork of the freezing tube. In this way the movement of the stirrer was guided and cramping prevented. The freezing tube consisted of a large test-tube of 80 c.c. capacity. The freezing tube was surrounded by a second glass tube giving an air space between the two of about a centimeter.

This outer tube was surrounded by the freezing mixture, which was contained in a large battery-jar wrapped with felt to prevent radiation.

The freezing mixture was varied to suit the conditions; the solutions of lower concentrations freezing with a mixture of salt and ice, while those of great concentrations often required the use of crystallized calcium chloride and ice.

By means of a small electric hammer uniform and gentle blows were delivered on the top of the thermometer during the time of an observation, thus overcoming the friction of the mercury in the capillary.

To facilitate the reading of the thermometer a small lens magnifying several diameters was employed, and more intense illumination of the thermometer scale was obtained by means of a small incandescent lamp. A thermometer graduated to tenths served to indicate the temperature of the freezing-mixture, the effort being made to keep this only a few degrees lower than the freezing temperature of the solution under observation.

Conductivity Apparatus.

The conductivity measurements were made by the well-known Kohlrausch method using the Wheatstone bridge, inductorium and telephone. Two types of cells were used. For the more dilute solutions the ordinary Arrhenius cell was employed, but for the very concentrated solutions a specially designed cell was employed. The accompanying sketch (Fig. 2) shows this cell in section.

The U-tube *AA* is 8 cm. in length and 2.8 cm. in diameter. The ground stoppers *BB* are filled with paraffine which serves to hold the tubes *cc* rigidly in place, thus insuring a constant distance between the electrodes. Each stopper is numbered corresponding to a number placed on the ends of the U-tube, so that the electrodes would not be interchanged. Furthermore, by means of fine vertical lines cut on each stopper and the necks of the U-tube, the electrodes could be returned to exactly the same positions each time. That there was no alteration in the distance between the electrodes was carefully established by a series of determinations of the cell constant on successive days, with the result that the differences were well within the limit of experimental error. The electrodes are of thick sheet platinum, and are 2.5 cm. in diameter.

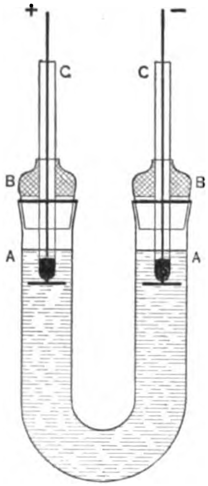

Fig. 2.

All of the conductivity measurements were made at 0°. The bath by which the solutions were maintained at this temperature was prepared in the following manner:

A glass battery-jar was filled with finely crushed, pure ice, to which was added a small volume of water. This jar was placed in a large water-bath, and the space between was packed with well-crushed ice. By this means it was found easy to maintain the solution in the conductivity cell to within one-tenth of a degree of the true zero. The ice in the battery jar was stirred occasionally, and the temperature of the bath was noted frequently, to insure the measurements being taken at 0.

At a later stage of the work it seemed very desirable to supplement the freezing-point and conductivity measurements with determinations of the boiling-point elevations and the refractive indices of some of the solutions. For the former determinations the boiling-point apparatus devised by Jones[1] was employed, while for the refraction measurements use was made of the well-known Pulfrich Refractometer.

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[1] Amer. Chem. Journ., 19, 581, 1897.

With the exception of the pipettes the volumetric apparatus used was specially made and carefully calibrated for this investigation.

The volumetric apparatus employed consisted of a series of measuring flasks and a burette and a series of pipettes. The pipettes were never used in making the dilutions.

SOLUTIONS.

The method of preparing the solutions varied somewhat according to the substance employed, but, in general, it may be said that a solution of two or three gram-molecular weights to the liter was first made, and from this, by successive dilutions, the less concentrated solutions were obtained. Wherever possible the mother-solution was made up by direct weighing. When this was not the case the solution was standardized either by gravimetric or volumetric methods.

Great care was taken to insure the accurate standardization of the mother-solution, and the dilutions were made with volumes large enough to minimize errors in burette readings and flask adjustments.

The water which was used as a solvent was of a high degree of purity. The ordinary tap-water was first distilled in the laboratory still, and then redistilled from a dilute solution of chromic acid. This second distillate was then distilled a third time according to the method of Jones and Mackay.[1] The water thus obtained was preserved in a large bottle which had previously been subjected to most careful cleaning. The water showed an average conductivity of 2.0×10^{-6}.

METHODS.

Freezing-point Method.

The practical details of the freezing-point method may be set forth most clearly by a description of the determination of the freezing-point of water, by which the zero-point of the thermometer was established prior to making any measurements upon solutions.

The freezing-tube was filled to a depth of 5 cm. with pure distilled water, and the thermometer and stirrer inserted. The tube was then placed in a vessel containing ice and salt, and the stirrer agitated frequently until ice separated. The tube was then removed and warmed until the ice just melted. It was then placed in the freezing-jacket, which was surrounded with finely-crushed dry ice to which has been added just enough salt to bring the temperature of the mixture to a few degrees below the freezing point of the solvent, in this case zero.

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[1] Amer. Chem. Journ., 19, 83, 1897.

The stirrer was agitated from time to time until freezing began, when the stirring was continued vigorously, and at the same time the electrical hammer was set in action. The thermometer scale was illumined by the incandescent lamp and the reading taken after the mercury column had remained stationary for about thirty seconds. It was almost always noticed that the solvent undercooled several degrees, and it was frequently necessary to add a small fragment of ice to induce freezing.

In the case of solutions the tendency to undercool was not so marked. Owing to the change in concentration due to the separation of ice, a correction was introduced. The determination of the freezing-point of the solvent as well as of any solution was repeated several times, and the mean of these results taken as the true freezing-point.

CONDUCTIVITY METHOD.

The solution was introduced into the conductivity cell, care being taken to avoid the collection of air bubbles on the electrodes, and the cell was then placed in the zero bath where it was allowed to remain for half an hour; this having been found to be sufficient time for the solution to acquire the uniform temperature of zero degrees. The conductivity was then determined by the well-known Kohlrausch method.

In the more concentrated solutions it was not found necessary to introduce a correction for the slight conductivity of the water.

BOILING-POINT METHOD.

Care was taken to use this method only on days when the barometer remained quite constant. The general method of carrying out a boiling-point measurement was employed, care being taken that the solutions boiled evenly, and that the thermometer was gently tapped before reading.

The boiling-point as recorded is in the mean of a series of readings taken at intervals of thirty seconds, and with each determination is recorded the corresponding barometric height.

REFRACTIVITY METHOD.

The determination of refractive indices was made with the refractometer of Pulfrich. Sodium light was employed and care was taken to have the solutions at uniform temperature. The readings were made to minutes of arc, and by means of the well-known formula $n = \sqrt{N^2 - \sin^2 X}$. The indices of refraction were calculated.

SOURCES OF ERROR.

In order to freeze solutions of relatively great concentrations it was found necessary to do away with the extra jackets used in working with dilute solutions. This source of error became manifest when the attempt was made to determine the freezing-points of solutions having concentrations less than half normal. This error diminishes as the concentration increases.

It was further found to be quite impossible to use more than 30 c.c. of solution; this limitation introducing another small source of error. The difficulty experienced in keeping at a minimum the difference between the temperature of the freezing-mixture and the freezing temperature of the solution was at times not slight. This was particularly noticeable when calcium chloride was used in the place of salt.

The correction introduced for the increase in concentration due to the separation of ice was the cause of some error. The amount of ice formed being a function of the degree of undercooling, it has been found practicable in working with dilute solutions to apply the correction formula $k = su/w$ to the observed depression.

In this formula s is the specific heat of the liquid, u the undercooling observed and w the latent heat of fusion of the solvent. The solution continues to lose heat even after freezing commences, and the heat lost is therefore greater than that measured by the undercooling, and the latent heat of fusion is less for a concentrated solution than for the pure solvent, so that for a given degree of undercooling there results a greater formation of ice than would result with the pure solvent.

This point has been tested experimentally by Loomis[1] while working with a 0.2 normal solution of sodium chloride. Applying the correction-formula his solution appeared concentrated about 0.2 per cent., whereas by actual determination of the change in concentration he found it to be concentrated 0.3 per cent. Such an error would be increased when the formula is applied to solutions varying from normal to three times normal. Furthermore, the amount of undercooling is found to vary greatly with the same solution upon successive freezings. It has been observed with almost every solution that the degree of undercooling is governed by the amount of over-warming. This same point was observed by Loomis.[2] He says: "Thus, one may effect almost any desired amount of overcooling by properly varying the degree of overwarming." Furthermore, as is well known, freezing can be induced by the introduction of a minute fragment of ice. Thus, it is evident that through this two-fold means of control of the degree of undercooling, some bias might be given to the results. The effort was made to avoid producing this error in the results. It must be stated, however, that this correction term is not entirely satisfactory, and that through its use some slight error has necessarily been introduced.

As has been stated two thermometers were employed in this investigation. One of these was graduated to fiftieths, while the other was divided into twentieths of a degree.

Estimation to hundredths of a degree was, therefore, the closest approximation that could be obtained.

The zero of the thermometer was determined just before making any measurements with the solutions.

The errors in the conductivity measurements were so slight that no record of them need be made. The refractivity measurements are affected by a slight error due to small inequalities of temperature throughout a series of determinations. This, while in general small, manifests itself in one or two of the curves to a noticeable extent.

The boiling-point method contains several sources of error. The platinum cylinder surrounding the thermometer bulb was found to cause some irregularity in the boiling-point of a concentrated solution, but to remove the cylinder introduces a two-fold error due to radiation and the cooled recondensed solvent.

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[1] Loomis, Phys. Rev.

nis, Phys. Rev.

Furthermore, the extremely low boiling-point constant for water renders the accuracy of the method in the more dilute solutions not very great. Of course the changes in barometric pressure also increase the difficulties in making an accurate boiling-point determination. This latter difficulty, it may be remarked, is greater in this locality than on the continent of Europe, where the barometric pressure remains practically constant for hours. The method gave so much trouble that it was temporarily discarded as being incapable of throwing much light on the problem in hand.

Tabulation of Results.

In the tables of freezing-point measurements the symbols employed have the following significance:

m = concentration in gram-molecular normal.

s = observed freezing-point depression.

k = correction for change in concentration due to separation of ice.

Δ = corrected freezing-point depression.

Δ/m = molecular freezing-point depression.

Wherever possible the results of other observers in the region of greater dilution are given, since, as has been stated, the method employed for concentrated solutions does not give highly accurate results when applied to dilute solutions.

In the tables of boiling-point measurements:

m = molecular concentration.

Δ' = rise of boiling-point.

In the tables of conductivity measurements v denotes the volume and μv the molecular conductivity at 0° C. In the tables of refractivity measurements the notation has the following meaning:

m = concentration in gram-molecular normal.

X = observed angle.

n = index of refraction.

The results are all expressed in curves (Figs. 3–13).

Hydrochloric Acid, HCl (36.46).

The hydrochloric acid used was found to be free from impurities. A solution of approximately three normal concentration was made up by means of the hydrometer. Its exact strength was then determined by diluting an appreciable volume one hundred times, and titrating successive portions by means of potassium hydroxide. The potassium hydroxide solution used had been carefully standardized against sulphuric acid, which, in turn, had been standardized gravimetrically by precipitation as barium sulphate. From the data thus obtained the mother-solution was diluted with the proper volume of water to make it exactly three times normal, and this dilution was then checked by a series of titrations.

From the mother-solution a series of dilutions were made, thus giving the solutions required. It may be well to state that these diluted solutions were preserved in hard-glass bottles, which had been thoroughly cleaned and steamed.

Freezing-point Measurements.

		Δ/m		
m	**Loomis.**[1]	**Jones.**[2]	**Barnes.**[3]	**Chambers & Frazer.**[4]
0.05	3.594		3.593	3.630
0.10	3.546	3.554	3.565	3.460
0.20	3.565		3.584	3.650
0.30	3.612			
0.40				3.760
m	*s*	*k*	Δ	Δ/*m*
1.0	4.140	0.018	4.122	4.122
1.5	6.720	0.087	6.633	4.422
2.0	10.218	0.281	9.937	4.969
2.5	13.510	0.055	13.455	5.382
3.0	18.100	0.004	18.096	6.030

Conductivity Measurements.

v.	2.000	1.000	0.667	0.500	0.400	0.333
μv.	216.50	200.32	182.35	170.19	152.38	141.87

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[1] PHYS. REV., 3, 276, 1896.

[2] Zeit. Phys. Chem., 12, 628, 1893.

[3] Trans. Roy. Soc. Can., Vol. VI., Sec. 50.

[4] Am. Chem. Jour. 23, 515, 1900.

Lithium Chloride, LiCl (42.48).

The concentration of the mother-solution of lithium chloride was determined volumetrically by means of a standard solution of silver nitrate.

The dilutions were made in the usual manner.

Owing to the limited supply of this salt it was impossible to carry the determinations beyond normal concentration.

Freezing-point Measurements.

m	s	k	Δ	Δ/m
0.06	0.250	0.010	0.240	4.067
0.12	0.450	0.010	0.440	3.667
0.24	0.865	0.003	0.862	3.592
0.59	2.245	0.003	2.242	3.800
1.18	4.800	0.001	4.799	4.066

Conductivity Measurements.

v.	16.95	8.47	4.22	1.67	0.88
μv.	53.75	50.42	46.76	42.28	35.58

Refractivity Measurements.

m	X	n
0.06	67° 22′	1.32438
0.12	67 16	1.32585
0.24	67 —	1.32711
0.59	66 21	1.33021
1.18	65 19	1.33526

Boiling-point Measurements.[1]

m	Δ'	Barom. Press.	Δ'/m
0.0135	0.130		0.960
0.2584	0.245	Constant.	0.950
0.5899	0.568		0.963
1.0500	1.063		1.010
1.6240	1.743		1.070

Ammonium Chloride, NH_4Cl (53.53).

The salt used was dried for several days in a desiccator over phosphorus pentoxide.

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[1] Biltz. Ztschr. phys. Chem., 40, 208, 1902.

The $3N$, $2N$ and N solutions were made up by direct weighing. The less concentrated solutions were made by diluting the normal solution. This method was pursued to avoid weighing such large masses of salt.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Biltz.[2]
0.04	3.50	3.39
0.05	3.48	
0.10	3.434	
0.20	3.396	
0.26		3.39
0.40	3.393	
0.54		3.41

m	s	k	Δ	Δ/m
1.0	3.75	0.020	3.730	3.730
2.0	7.55		7.550	3.775
3.0	11.70		11.700	3.900

Conductivity Measurements.

v.	5.0	2.0	1.0	0.5	0.333
μv.	68.94	66.15	64.35	59.27	58.61

Refractivity Measurements.

m	X	n
0.2	66° 55′	1.32750
0.5	66 18	1.33045
1.0	65 15	1.33559
2.0	63 20	1.34536
3.0	61 30	1.35508

Sodium Chloride, NaCl (58.50).

The sodium chloride used was prepared from ordinary salt by precipitation from concentrated solution by means of hydrochloric acid gas. The salt thus obtained was washed with a little cold water, and was then dried at 120° C in an air bath.

The 3N, 2N and N solutions were made up by direct weighing, the latter serving as the mother-solution for the lesser concentrations.

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[1] PHYS. REV., 3, 276, 1896.

[2] Ztschr. Phys. Chem., 40, 198, 1902.

Freezing-point Measurements.

	Δ/m			
m	**Loomis.**[1]	**Jones.**[2]	**Biltz.**[3]	**Kahlenberg.**[4]
0.05	3.531	3.52	3.41	——
0.06	3.529	——	——	——
0.07	3.510	——	——	——
0.08	3.501	——	——	——
0.09	3.494	——	——	——
0.10	3.484	3.47	3.47	3.26
0.20	3.439	3.42	3.44	——
0.26	——	——	——	3.19
0.30	——	——	——	3.21
0.40	——	——	3.42	——
0.50	——	——	——	3.24

m	s	k	Δ	Δ/m
0.5	1.760	0.001	1.759	3.518
1.0	3.550	0.004	3.546	3.546
2.0	7.470	0.003	7.467	3.734
3.0	12.225	0.002	12.223	4.074

Conductivity Measurements.

v.	5.000	2.000	1.000	0.500	0.333
μv.	51.84	48.62	47.16	43.14	36.59

Refractivity Measurements.

m	X	n
0.2	67° 1′	1.32703
0.5	66 24	1.32997
1.0	65 26	1.33469
2.0	63 37	1.34389
3.0	61 59	1.35249

Boiling-point Measurements.[5]

m	Δ′	**Barom. Press.**	Δ′/m
0.1256	0.195	754.0 mm.	1.552
0.2500	0.390	"	1.160
0.3793	0.598	"	1.576
0.5046	0.820	"	1.625
0.6299	1.031	"	1.637
0.8792	1.474	"	1.677
1.1409	1.970	"	1.726
2.0130	4.471	743.5	2.221
3.1242	6.820	743.4	2.183

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[1] Phys. Rev., I., 279, 1893.

[2] Zeit. Phys. Chem., 11, 110, 1893.

[3] Ibid., 40, 199, 1902.

[4] Jour. Phys. Chem., 5, 353, 1901.

[5] Kahlenberg, Jour. Phys. Chem., 5, 362, 1901.

Potassium Chloride, KCl (74.60).

The salt used was prepared by repeated crystallization from fairly pure specimens. It was then dried for several days in an air-bath at 110° C. and afterwards preserved in a desiccator over calcium chloride until it was used.

From the mother-solution prepared by direct weighing, the lesser concentrations were obtained by dilution.

Freezing-point Measurements.

	Δ/m		
m	Loomis.[1]	Jones.[2]	Biltz.[3]
0.05	3.50	3.50	—
0.10	3.445	3.47	3.47
0.20	3.404	—	—
0.30	—	—	3.41
0.40	3.353	—	—
0.50	—	—	3.34
0.80	—	—	3.27

m	s	k	Δ	Δ/m
0.2	0.688	0.003	0.685	3.425
0.5	1.695	0.003	0.692	3.384
1.0	3.400	—	3.400	3.400
2.0	6.950	0.006	6.944	3.472
3.0	11.065	0.003	11.062	3.687

Conductivity Measurements.

v.	20.0	10.0	5.0	2.0	1.0	0.5
μv.	72.37	69.53	68.71	65.21	61.07	60.98

Boiling-point Measurements.[4]

m	Δ'	Barom. Press.	Δ'/m
0.2122	0.293	737.6 mm.	1.381
0.5124	0.700	"	1.366
0.9012	1.247	"	1.383
1.3990	2.004	"	1.432
2.0170	2.975	"	1.475
2.4160	3.653	"	1.512
2.7720	4.266	"	1.539
3.1840	5.009	"	1.570

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[1] PHYS. REV., 3, 276, 1896.

[2] Ztschr. phys. Chem., 11, 11

[3] Ibid., 40, 198, 1902.

[4] Kahlenberg, Jour. Phys. Che

Calcium Chloride, $CaCl_2$ (110.8).

The salt was obtained in a well-crystallized condition. It was dissolved in enough water to insure the solution having a concentration of at least 2.5N. By means of several gravimetric determinations of calcium the exact strength of the mother-solution was obtained. It was then diluted to 2.5N and the calcium redetermined as a check. From this mother-solution the other solutions were prepared by dilution.

It may be noted at this point that owing to the extremely large depressions produced by concentrated solutions of this substance, it was necessary to employ crystallized calcium chloride and ice as the freezing mixture.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones & Chambers.[2]
0.05	4.85	
0.10	4.80	4.98
0.20	4.84	4.96
0.30		5.02
0.40		5.16
0.50	5.19	5.26

m	s	k	Δ	Δ/m
1.0	6.350	0.005	6.345	6.345
1.5	11.300	0.004	11.296	7.531
2.0	17.875	0.008	17.867	8.934

Conductivity Measurements.

v.	1.000	0.667	0.500	0.400
μv.	71.16	62.14	53.98	44.79

Strontium Chloride, $SrCl_2$ (158.5).

The salt was purified by repeated crystallizations, and finally dried at 110° C. It was preserved in a desiccator over calcium chloride until used.

The mother-solution was made up by direct weighing, and then analyzed for both strontium and chlorine as a check. The dilutions were made in the usual manner.

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[1] Phys. Rev., 4, 298, 1897.

[2] Amer. Chem. Jour., 23, 93, 1900.

Freezing-point Measurements.

	$\Delta'm$	
m	**Loomis.**[1]	**Jones & Chambers.**[2]
0.05	4.90	5.16
0.10	4.85	4.88
0.20	4.82	4.87
0.30		4.90
0.40		4.95
0.50	5.08	5.09

m	s	k	Δ	Δm
1.0	6.010	0.010	6.000	6.000
1.5	10.725		10.725	7.150
2.0	16.425	0.003	16.422	8.211

Conductivity Measurements.

$v.$	2.000	1.000	0.667	0.500
$\mu v.$	84.26	74.57	63.01	55.26

Barium Chloride, $BaCl_2$ (208.3).

The salt was obtained in a relatively pure condition. It was recrystallized several times, and then dried for some hours at 110° C. in the air-bath.

The mother-solution was made up by direct weighing and the lesser concentrations obtained by dilution. The slight solubility of the salt prevented the study of concentrations beyond 0.75N.

Freezing-Point Measurements.

	$\Delta'm$	
m	**Loomis.**[3]	**Jones & Chambers.**[4]
0.05	4.770	
0.10	4.690	4.85
0.20	4.655	4.77
0.30		4.82
0.50	4.830	4.95

m	s	k	Δ	$\Delta'm$
0.5	2.500	0.007	2.493	4.986
0.75	3.860	0.003	3.857	5.143

Conductivity Measurements.

v	20.000	10.000	4.000	2.000	1.333
μv	116.05	103.79	95.94	89.24	85.27

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[1] PHYS. REV., 4, 287, 1897.

[2] Amer. Chem. Jour., 23, 94, 1902.

[3] PHYS. REV., 3, 277, 1896.

[4] Amer. Chem. Jour., 23, 94, 1900.

Boiling-point Measurements.[1]

m	Δ'	Barom. Press.	Δ'/m
0.3397	0.208	752.8 mm.	0.612
0.8290	0.496	"	0.598
1.3612	0.839	"	0.616
1.9868	1.293	"	0.651
2.7071	1.909	"	0.705
3.5036	2.517	"	0.718

Nitric Acid, HNO_3 (63.05).

By means of the hydrometer and Lunge's tables a solution of approximately 3N was made up. This solution was then accurately standardized by means of potassium hydroxide, the same method being used as in the case of hydrochloric acid.

From the mother-solution thus prepared, the more dilute solutions were obtained.

Freezing point Measurements.

	Δ/m	
m	Jones.[2]	Loomis.[3]
0.05	3.71	3.51
0.10	3.53	3.50
0.20		3.48

m	s	k	Δ	Δ/m
0.5	1.840	0.018	1.822	3.644
1.0	3.850	0.054	3.796	3.796
1.5	5.980	0.042	5.938	3.959
2.0	8.425	0.015	8.410	4.205
2.5	11.125	0.079	11.046	4.418
3.0	14.058	0.150	13.908	4.636

Conductivity Measurements.

$v.$	2.000	1.000	0.667	0.500	0.400	0.333
$\mu v.$	213.30	194.95	184.89	169.23	155.43	140.97

Lithium Nitrate, $LiNO_3$ (69.07).

The sample of lithium nitrate used was obtained in well-crystallized form. It was heated to 120° C. for several days in an air-bath, and was then allowed to cool in a desiccator over calcium chloride. When cool, the mother-solution was prepared by direct weighing of the salt, care being taken to make the weighing as quickly as possible after the removal of the salt from the desiccator.

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[1] Kahlenberg, Jour. Phys. Chem., 5, 366, 1901.

[2] Zeit. Phys. Chem., 12, 623, 1893.

[3] PHYS. REV. 4, 282, 1897.

Owing to the limited supply of this salt the mother-solution contained only one gram-molecule of dissolved substance in a liter.

Freezing-point Measurements.

m	s	k	Δ	Δ/m
0.05	0.185	0.002	0.183	3.660
0.10	0.355	0.002	0.353	3.530
0.20	0.745	0.023	0.722	3.610
0.30	1.095	0.001	1.094	3.647
0.40	1.465	0.003	1.462	3.655
0.50	1.860	0.005	1.855	3.710
0.60	2.275	0.008	2.267	3.778
0.70	2.665	0.002	2.663	3.804
0.80	3.135		3.135	3.919
0.90	3.560	0.003	3.557	3.952

Conductivity Measurements.

v.	20.00	10.00	5.00	3.33	2.50	2.00	1.67	1.43	1.25	1.11
μv.	50.00	47.56	45.91	44.05	43.90	42.50	40.81	39.91	39.89	37.74

Ammonium Nitrate, NH_4NO_3 (80.12).

The salt was obtained in a comparatively pure condition, and was recrystallized several times. It was then dried at 100° C. and preserved until needed in a desiccator over calcium chloride.

The mother-solution was prepared by direct weighing, and from it the successive dilutions were made.

Freezing-point Measurements.

	Δ/m
m	Loomis.[1]
0.025	3.49
0.050	3.47
0.100	3.424
0.200	3.321

m	s	k	Δ	Δ/m
0.5	1.690	0.004	1.686	3.372
1.0	3.150	0.005	3.145	3.148
2.0	6.000	0.004	5.996	2.998
3.0	8.725	0.005	8.720	2.906

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[1] PHYS. REV., 3, 279, 1896.

Conductivity Measurements.

v.	20.0	10.0	5.0	2.0	1.0	0.5
μv.	67.49	65.05	63.44	60.26	54.97	52.81

Refractivity Measurements.

m	X	n
0.05	67° 22′	1.32538
0.10	67 21	1.32585
0.20	67 3	1.32687
0.50	66 25	1.32989
1.00	65 24	1.33485
2.00	63 30	1.34449

Sodium Nitrate, $NaNO_3$ (85.09).

The sample of sodium nitrate used was purified by repeated crystallizations. The purified salt was dried at 110° C. in an air-bath, and preserved over calcium chloride in a desiccator until required.

The mother-solution was made up by direct weighing, and the other solutions obtained from this by dilution.

Freezing-Point Measurements.

	Δ/m
m	Loomis.[1]
0.05	3.44
0.10	3.428
0.20	3.345

m	s	k	Δ	Δ/m
1.0	3.200	0.002	3.198	3.198
1.5	4.670	0.001	4.669	3.113
2.0	6.150	0.003	6.147	3.074
2.5	7.470	0.002	7.468	2.987
3.0	8.913	0.004	8.909	2.969

Conductivity Measurements.

v.	2.000	1.000	0.667	0.500	0.400
μv.	44.90	40.41	36.90	34.16	30.96

Potassium Nitrate, KNO_3 (101.19).

The specimen of potassium nitrate was obtained in a fair state of purity. This was recrystallized until it no longer gave a flame-test for sodium. It was then dried for several days at 110° C. in an air-bath, after which it was preserved in a desiccator over calcium chloride until required for use.

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[1] Phys. Rev., 3, 279, 1896.

The mother-solution was made up by direct weighing, and the remaining solutions made by dilution.

Freezing-point Measurements.

	Δ/m
m	Loomis.[1]
0.05	3.41
0.10	3.314
0.20	3.194

m	s	k	Δ	Δ/m
0.4	1.295	0.037	1.258	3.145
0.5	1.553	0.016	1.537	3.074
1.0	2.730	0.001	2.729	2.729

Conductivity Measurements.

v.	2.000	1.000	0.667
μv.	53.20	49.97	46.30

Boiling-point Measurements.[2]

m	Δ'	Barom. Press.	Δ'/m
0.2789	0.248	741.1 mm.	0.889
0.6058	0.518	"	0.855
0.9721	0.822	"	0.845
1.4798	1.207	"	0.815
2.1333	1.706	741.2	0.795
2.7095	2.123	"	0.783

Sulphuric Acid, H_2SO_4 *(98.08).*

The acid used was free from the ordinary impurities.

By means of the hydrometer and Lunge's tables a solution approximately 3N was made up. A portion of this solution was then diluted a hundred times, and successive portions of this diluted solution were removed for titration with N/5 potassium hydroxide. After the exact strength of the solution was ascertained, it was diluted sufficiently to make the solution strictly 3N.

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[1] Phys. Rev., 3, 278, 1896.

[2] Kahlenberg, Jour. Phys. Chem., 5, 368, 1901.

This solution was then checked by several titrations. As has been said the potassium hydroxide solution used for the titration was standardized by means of N/5 sulphuric acid, which had been standardized gravimetrically.

The dilutions were made as usual from the mother-solution.

Freezing-point Measurements.

	Δ/m			
m	**Loomis.**[1]	**Jones.**[2]		**Barnes.**[3]
0.05	4.130			4.167
0.10	3.968	3.945		3.961
0.20	3.850			3.883
m	*s*	*k*	Δ′	Δ/*m*
0.10	0.413	0.016	0.397	3.970
0.30	1.180	0.024	1.156	3.853
0.50	2.040	0.023	2.017	4.034
1.00	4.203	0.014	4.189	4.189
1.50	7.450	0.007	7.443	4.962
2.00	11.300	0.004	11.296	5.648
2.50	16.275		16.275	6.510

Conductivity Measurements.

v.	2.000	1.000	0.667	0.500	0.400	0.333	0.286	0.250	0.222	0.200
uv.	277.30	253.44	221.25	199.42	178.79	155.29	135.00	118.86	100.21	86.97

Ammonium Sulphate, $(NH)_2SO_4$ *(114.14).*

The salt used was purified by several recrystallizations. It was dried at 100° C. in an air-bath, and was then preserved in vacuo over sulphuric acid until required.

The mother-solution was made up by direct weighing, and the lesser concentrations obtained by dilution.

Freezing-point Measurements.

m	*s*	*k*		/*m*
0.05	0.025	0.001	0.024	4.80
0.10	0.475	0.006	0.469	4.69
0.20	0.825	0.007	0.818	4.09
0.50	1.975	0.006	1.969	3.94
1.00	3.725	0.039	3.686	3.69
1.40	5.200	0.067	5.133	3.67

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[1] Phys. Rev., I., 281, 1893.

[2] Ztschr. phys. Chem., 12, 628, 1893.

[3] Trans. Roy. Soc. Canada, Vol. VI., Sec. III., 50.

Conductivity Measurements.

v.	20	10	5	2	1	0.71
μv.	100.60	95.84	86.15	80.08	72.55	69.30

Refractivity Measurements.

m	X	n
0.05	67° 15′	1.32593
0.10	67	1.32711
0.20	66 45	1.32829
0.50	65 42	1.33338
1.00	64 7	1.34131
1.40	62 49	1.34807

Sodium Sulphate, Na_2SO_4 (142.16).

The salt used was in the form of the decahydrate.

It was heated to 120° C. for several days, and was then removed from the air bath and finely pulverized in a mortar, after

Freezing-point Measurements.

	Δ/m
m	Loomis.[1]
0.05	4.590
0.10	4.340
0.20	4.071
0.30	3.875

m	s	k	Δ	Δ/m
0.50	1.850	0.011	1.839	3.678

Conductivity Measurements.

v.	20.0	10.00	5.00	2.00	1.00	0.67	0.50
μv.	93.06	84.92	73.09	60.54	47.13	36.82	28.54

Refractivity Measurements.

m	X	n
0.05	67° 13′	1.32609
0.10	66 58	1.32727
0.20	66 30	1.32949
0.50	65 20	1.33518
1.00	63 37	1.34389
1.50	62 05	1.35195
2.00	60 43	1.35934

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[1] Phys. Rev., 3, 277, 1896.

which it was placed over sulphuric acid in a vacuum desiccator until required. The mother-solution was made up by direct weighing.

Owing to the formation of the hydrate upon cooling, it was found impossible to extend the observations on the freezing-point beyond N/2 concntration.

Boiling-point Measurements.

m	Δ'	**Barom. Press.**	Δ'/m
0.05	0.050	763.0 mm.	1.00
0.10	0.105	763.1	1.05
0.20	0.235	763.3	1.17
0.50	0.531	763.5	1.06
1.00	1.064	763.5	1.06
1.50	1.748	765.0	1.07
2.00	2.085	764.8	1.04

Potassium Sulphate, K_2SO_4 (174.06).

The specimen of salt used was dried for several days in the air-bath at a temperature of 120° C., and was then preserved in a desiccator over sulphuric acid until required.

Freezing-point Measurements.

	Δ/m	
m	**Loomis.**[1]	**Jones.**[2]
0.05	4.540	4.61
0.10	4.317	4.28
0.20	4.067	
0.30	3.891	

Conductivity Measurements.

v.	20	10	5	2
μv.	118.89	109.79	98.88	88.93

Refractivity Measurements.

m	X	n
0.05	67° 12′	1.32616
0.10	66 57	1.32735
0.20	66 30	1.32949
0.50	65 20	1.33518

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[1] Phys. Rev., 3, 277, 1896.

[2] Ztschr. phys. Chem., 11, 527, 1893.

The mother-solution was made up by direct weight.

Owing to the excessively slight solubility of this salt it was impossible to extend the freezing-point observations beyond $\frac{3}{10}$N.

It is also worthy of note at this point that the refractive indices for solutions of sodium and potassium sulphates are nearly identical, as may be seen from the curves.

Sodium Carbonate, Na_2CO_3 (*106.1*).

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.05	4.640	4.67
0.10	4.416	4.45
0.20	4.170	

m	s	k	Δ	Δ/m
0.5	1.883	0.001	1.882	3.764

Conductivity Measurements.

$v.$	20	10	5	2	1	0.5
$\mu v.$	85.80	76.80	66.90	53.10	39.14	24.53

Refractivity Measurements.

m	X	n
0.05	67° 14′	1.32601
0.10	66 57	1.32735
0.20	66 29	1.32957
0.50	65 12	1.33584
1.00	63 20	1.34536
2.00	60 13	1.36209

Boiling-point Measurements.

m	Δ'	Barom. Pressure.	Δ'/m
0.05	0.053	763.5 mm.	1.060
0.10	0.132	763.7	1.320
0.20	0.258	763.8	1.290
0.50	0.538	764.3	1.176
1.00	0.947	765.3	0.947
2.00	1.747	771.5	0.874

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[1] [illegible] REV., 3, 278, [illegible]

[2] [illegible] phys. Chem., [illegible] 1893.

The salt was dried for twenty-four hours over sulphuric acid in vacuo. The solutions were made up by direct weighing and dilution. Owing to the separation of the hydrate, freezing-point measurements beyond 0.2N were impossible.

Potassium Carbonate, K_2CO_3 *(138.3).*

Freezing-point Measurements.

	Δ/m	
m	**Loomis.**[1]	**Jones.**[2]
0.05	4.710	4.75
0.06		4.75
0.10	4.540	4.62
0.20	4.385	

m	s	k	Δ	Δ/m
0.4	1.728	0.045	1.683	4.208
1.0	4.383	0.008	4.375	4.375
2.0	9.725	0.015	9.710	4.855

Conductivity Measurements.

$v.$	20	10	5	2.5	1	0.5
$\mu v.$	114.04	104.34	95.54	87.05	74.25	61.57

Refractivity Measurements.

m	X	n
0.05	67° 10′	1.32632
0.10	66 54	1.32758
0.20	66 26	1.32980
0.40	65 35	1.33395
1.00	63 18	1.34553
2.00	60 12	1.36219

Boiling-point Measurements.

m	Δ'	**Barom. Press.**	Δ'/m
0.05	0.055	765.5 mm.	1.100
0.10	0.102	765.5	1.020
0.20	0.194	765.2	0.970
0.40	0.378	765.0	0.945
1.00	1.080	764.5	1.080
2.00	2.680	764.5	1.340

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[1] PHYS. REV., 3, 278, 1896.

[2] Ztschr. phys. Chem., 12, 623, 1893.

The specimen used was dried for six days in vacuo over sulphuric acid. The mother-solution was made up by direct weighing and the lesser concentrations were obtained by dilution.

Phosphoric Acid, H_3PO_4 *(98.03).*

The acid was obtained in a well-crystallized condition. It was dissolved in pure water and the strength of the solution determined by means of gravimetric analysis, the phosphoric acid being weighed as magnesium pyrophosphate.

The analysis was checked by means of a pyknometric determination of its specific gravity.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.05	2.490	
0.06		2.65
0.10	2.358	2.35
0.15		2.32
0.20	2.249	

m	s	k	Δ	Δ/m
0.52	1.138	0.027	1.111	2.137
1.04	2.475	0.007	2.468	2.373
2.08	5.408	0.010	5.398	2.595
3.12	9.463	0.008	9.455	3.030

Conductivity Measurements.

v.	15.39	7.68	3.85	1.92	0.96	0.48	0.32
μv.	82.18	62.06	50.38	42.92	37.70	34.89	33.16

Refractivity Measurements.

m	X	n
0.065	67° 18′	1.32570
0.130	67 12	1.32616
0.260	66 55	1.32750
0.520	66 30	1.32949
1.040	65 39	1.33362
2.080	64 00	1.34191
3.120	62 30	1.34974

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[1] PHYS. REV., 3, 279, 1896.

[2] Ztschr. phys. Chem., 12, 623, 1893.

Here, as in all similar cases, care was taken to dilute an appreciable volume of the mother-solution, and to employ a large volume of the diluted solution for the analysis. From the standardized mother-solution the lesser concentrations were obtained by dilution.

Potassium Di-hydrogen Phosphate, KH_2PO_4 (136.17).

The specimen used was dried in an air-bath for three days at 100° C. and was then preserved in vacuo over sulphuric acid. The mother-solution was made up by direct weighing and the lesser concentrations obtained by dilution.

Owing to the slight solubility of the salt it was found to be impossible to extend the freezing-point measurements beyond normal concentration.

Freezing-point Measurements.

	Δ/m
m	Loomis.[1]
0.01	3.58
0.02	3.60
0.05	3.48
0.10	3.37
0.20	3.22

m	s	k	Δ	Δ/m
0.5	1.525		1.525	3.050
1.0	2.800	0.020	2.780	2.780

Conductivity Measurements.

v.	20.0	10.0	5.0	2.0	1.0	0.667
$v\mu$.	51.00	46.71	42.45	38.24	32.21	26.98

Refractivity Measurements.

m	X	n
0.05	67° 15′	1.32593
0.10	67 00	1.32711
0.20	66 45	1.32829
0.50	65 50	1.33272
1.00	64 25	1.33978
1.50	63 10	1.34623

---

[1] Phys. Rev., 4, 284, 1897.

Sodium Hydroxide, NaOH (40.06).

The mother-solution of sodium hydroxide was made from a chemically pure specimen. The exact strength of the solution was determined by titration with N/5 sulphuric acid, care being taken to work with volumes sufficiently large to minimize errors in dilution and burette readings. The more dilute solutions were prepared by diluting the mother-solutions. The solutions were used as soon as possible after preparation to avoid error, owing to the solvent action of the alkali on the glass of the containing bottles, and to the absorption of carbon dioxide from the air.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.02	3.46	
0.05	3.45	3.56
0.10	3.41	3.42
0.20	3.41	-

m	*s*	*k*	Δ	Δ/*m*
0.52	2.175	0.026	2.149	3.466
1.24	4.492	0.043	4.449	3.588
1.86	7.175	0.036	7.139	3.838
2.48	9.775	0.010	9.765	3.937

Conductivity Measurements.

v.	16.0	8.0	2.0	0.81	0.54	0.40
μv.	117.00	115.00	104.00	93.46	80.08	71.43

Potassium Hydroxide, KOH (56.0).

Chemically pure potassium hydroxide from alcohol was used in the preparation of the mother-solution. The concentration of this original solution was determined by titration with N/5 sulphuric acid, and the dilutions made in the usual manner. The same precautions were taken as with sodium hydroxide, to prevent the solutions from becoming contaminated with silicates and carbonates.

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[1] Phys. Rev., 4, 282, 1897.

[2] Ztschr. phys. Chem., 12, 623, 2893.

Freezing-point Measurements.

m	Δ/m Loomis.[1]	Δ/m Jones.[2]
0.05	3.44	3.58
0.10	3.43	3.47
0.20	3.43	

m	s	k	Δ	Δ/m
0.5	1.810	0.002	1.808	3.616
1.0	3.920	0.039	3.881	3.881
1.5	5.975	0.011	5.964	3.976
2.0	8.492	0.006	8.486	4.243
2.5	11.308	0.006	11.302	4.521

Conductivity measurements.

v.	16.0	8.0	2.0	1.0	0.667	0.500	0.400
μv.	125.30	122.80	118.40	113.33	106.35	101.15	97.40

Fig. 3.

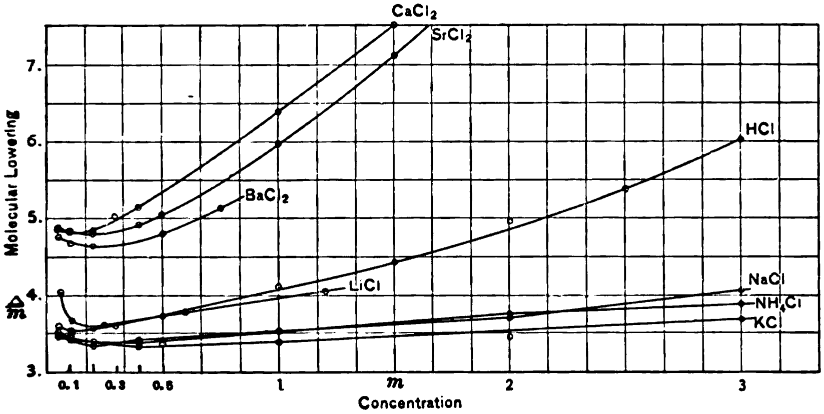
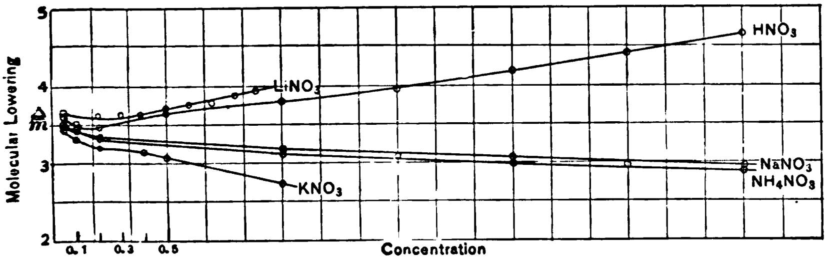


Fig. 4.



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[1] Phys. Rev., 4, 282, 1897.

[2] Ztschr. phys. Chem., 12, 623, 1893.

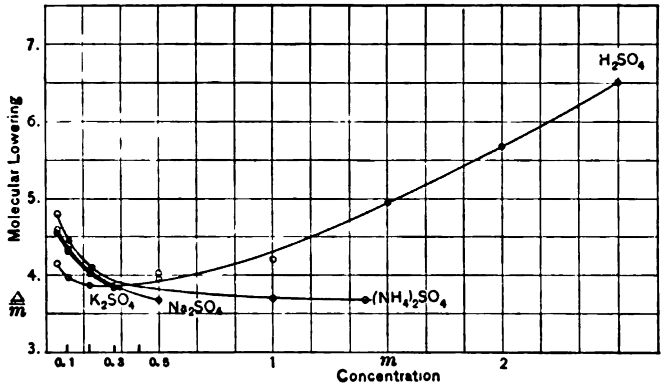

7.
6.
5.
4.
3.
Molecular Lowering
$\frac{\Delta}{m}$
H₂SO₄
K₂SO₄
Na₂SO₄
(NH₄)₂SO₄
0.1
0.3
0.5
1
m
2
Concentration

Fig. 5.

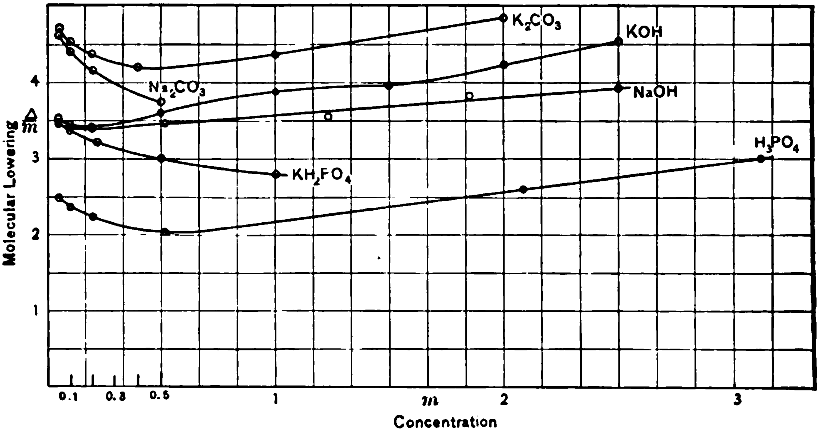
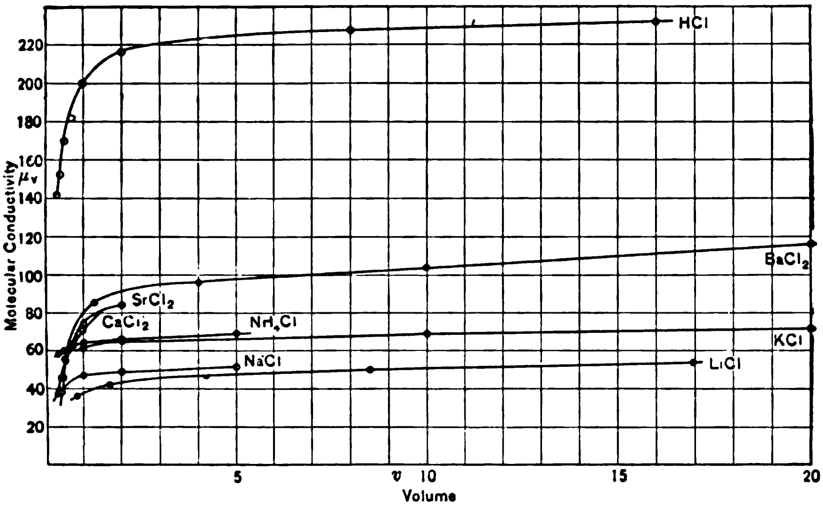
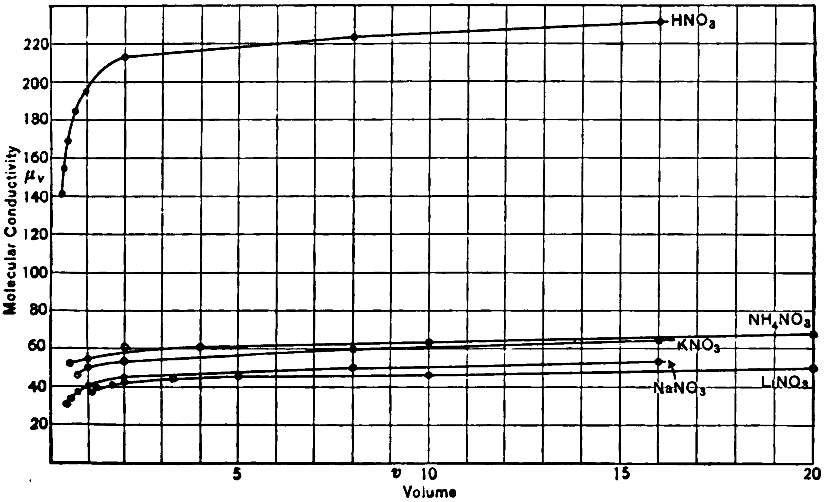

4
$\frac{\Delta}{m}$
3
2
1
Molecular Lowering
K₂CO₃
KOH
Na₂CO₃
NaOH
H₃PO₄
KH₂FO₄
0.1
0.3
0.5
1
m
2
3
Concentration

Fig. 6.



Molecular Conductivity
μ_v
220
200
180
160
140
120
100
80
60
40
20
5
v 10
15
20
Volume
HCl
BaCl$_2$
SrCl$_2$
CaCl$_2$
NH$_4$Cl
KCl
NaCl
LiCl

Fig. 7.



Molecular Conductivity
μ_v
220
200
180
160
140
120
100
80
60
40
20
5
v 10
15
20
Volume
HNO$_3$
NH$_4$NO$_3$
KNO$_3$
NaNO$_3$
LiNO$_3$

Fig. 8.

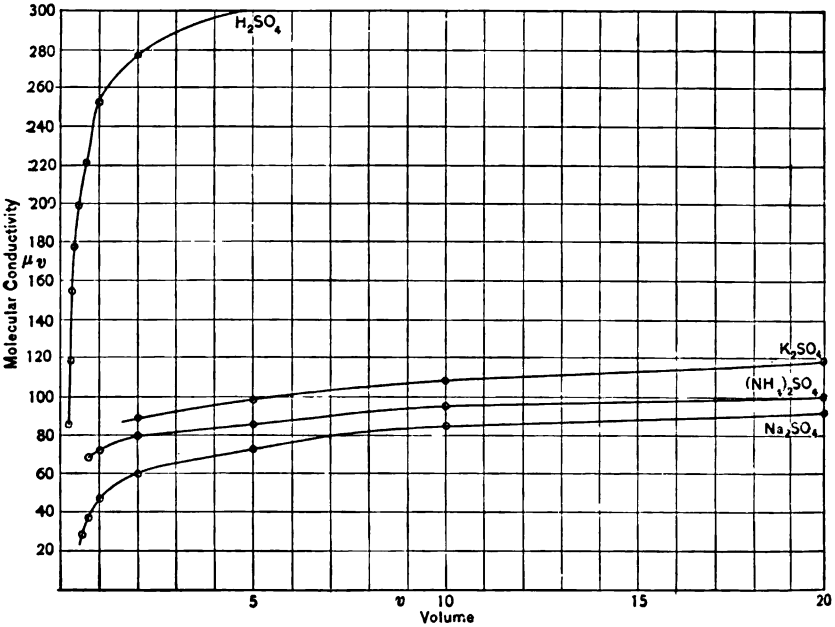

Molecular Conductivity
μv
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
H_2SO_4
K_2SO_4
$(NH_4)_2SO_4$
Na_2SO_4
5
v 10
15
20
Volume

Fig. 9.

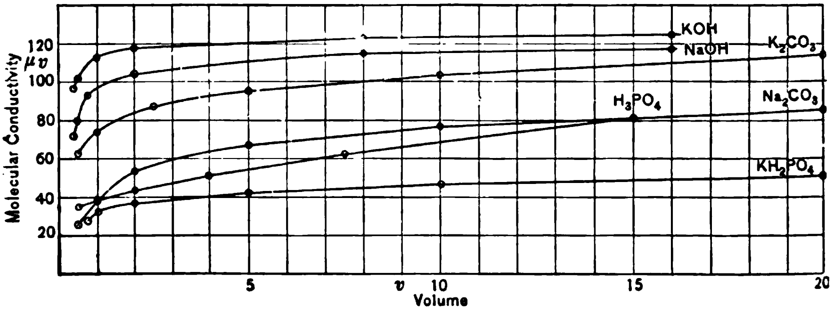

Molecular Conductivity
μv
120
100
80
60
40
20
KOH
NaOH
K_2CO_3
H_3PO_4
Na_2CO_3
KH_2PO_4
5
v 10
15
20
Volume

Fig. 10.

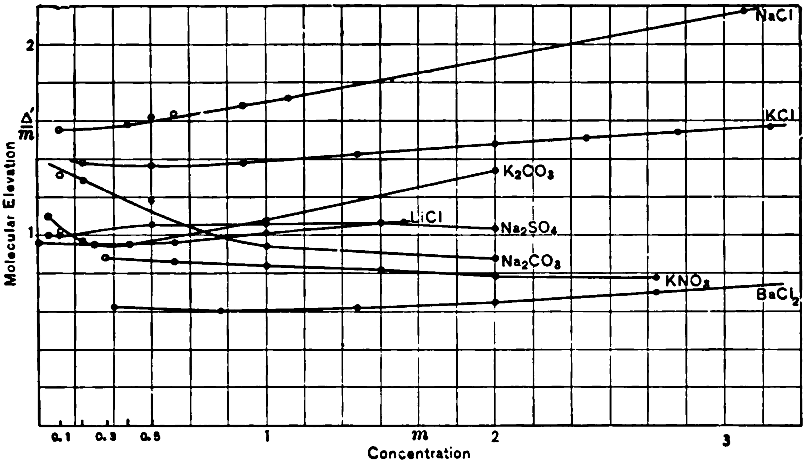

2
$\frac{\Delta'}{m}$
1
Molecular Elevation
NaCl
KCl
K_2CO_3
LiCl
Na_2SO_4
Na_2CO_3
KNO_3
$BaCl_2$
0.1
0.3
0.5
1
m
2
3
Concentration

Fig. 11.

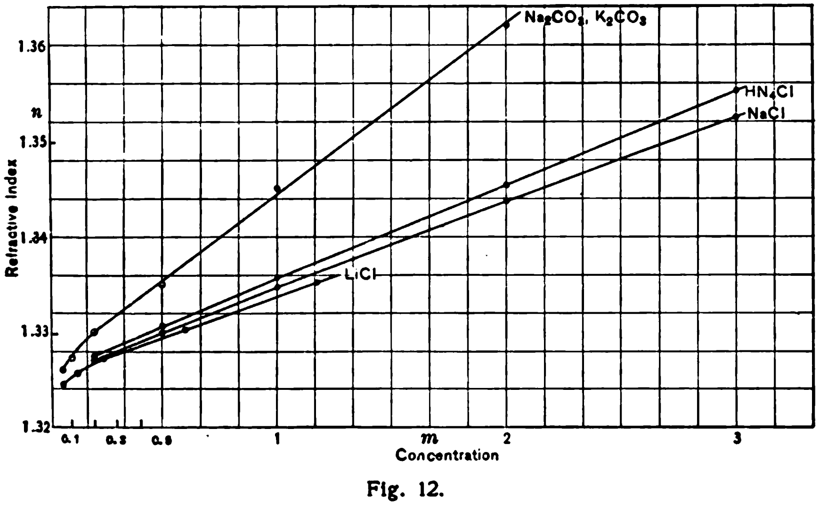

1.36
n
1.35
1.34
1.33
1.32
Refractive Index
Na_2CO_3, K_2CO_3
HN_4Cl
NaCl
LiCl
0.1
0.3
0.5
1
m
2
3
Concentration

Fig. 12.

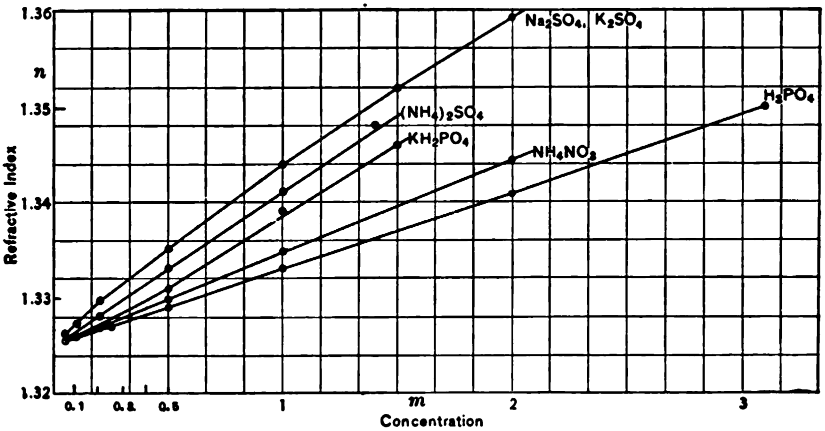


Fig. 13.

SUMMARY.

From the work that was done previous to this investigation, and from the data here presented, it is seen that with but few exceptions electrolytes in general give abnormal molecular depressions of the freezing-point in concentrated solutions. Among these exceptions are sodium, potassium and ammonium nitrates, and potassium dihydrogen phosphate.

Among the chlorides we observe that those of the second group in the periodic system give greater molecular depressions than those of the first group. We also observe that the curve for hydrochloric acid lies considerably above the corresponding curves for lithium, ammonium, sodium and potassium chlorides. The relation between lithium and the members of the second group is clearly shown by the curves for lithium chloride and lithium nitrate, which resemble the curves for the corresponding salts in the second group more closely than the analogues of the first group. The relation is very marked in the case of lithium nitrate.

Owing to limited solubility the study of the sulphates at great concentration was not possible, so that it cannot be stated whether or not these salts exhibit the phenomenon.

In general we may say that the freezing-point curve for any acid lies above those of the salts which it forms with the metals of the first group, while it lies below the curves for its second group salts. Further, it will be seen that the molecular depressions for similar substances are arranged in the order of their molecular weights. The conductivity curves for all of the substances studied are perfectly normal throughout, showing absolutely no peculiarities in the region of dilution where the minimum of molecular depression manifests itself. The refractivity curves are nearly straight lines. In the few boiling-point curves which are given there is a more or less marked minimum, but as has already been pointed out, no great reliance can be placed upon the results obtained by the boiling-point method.

CONCLUSION.

The results obtained in this investigation can all be explained satisfactorily by the suggestion put forward by Jones and Chambers. We have attempted other explanations. The nature of many of the freezing-point curves suggests the curves obtained by Amagat[1] for gases. To these freezing-point curves we attempted to apply the well-known equation of Van der Waals:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

It, however, soon became obvious that without some radical modifications this equation could not be used.

Other suggestions met the same fate when tested by the experimentally established facts.

It should be added that the boiling-point determinations, as far as they have any value, point to the correctness of the suggestion that there are *hydrates formed in concentrated solutions.* The boiling-point curves show a minimum corresponding to the freezing-point curves. *The minimum in the boiling-point curves, however, is at greater concentration than in the freezing-point curves.* This is just what we should expect if the suggestion of the existence of hydrates in such solutions was correct. At the higher temperature the hydrates would be less stable, and would require greater concentration for their formation than at the lower temperature.

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[1] Ann. Chim. Phys. [5], 19, 379, 1880.

Another strong line of evidence in favor of the existence of hydrates in concentrated solutions of electrolytes is the relation between the *water of crystallization* and the magnitude of the abnormal freezing-point lowerings. If hydrates exist in such solutions we should expect *those substances that crystallize with the greatest amount of water to be the ones that would form in solution the most complex hydrates.* That such is, in general, the fact, can be seen at once from Figs. 3, 4 and 5. Take Fig. 3, the chlorides of potassium, ammonium and sodium have no water of crystallization and give smaller lowering of the freezing-point of water than lithium chloride which crystallizes at low temperatures with two molecules of water; lithium chloride, in turn gives smaller lowering of the freezing-point than barium chloride which crystallizes at ordinary temperatures with two molecules of water. The chlorides of calcium and strontium, each with six molecules of water of crystallization, give still greater lowering of the freezing-point of water.

When we turn to Fig. 4, similar relations appear. Potassium, ammonium and sodium nitrates have no water of crystallization and all show comparatively small lowering of the freezing-point of water. Lithium nitrate with two and one half molecules of water of crystallization gives much greater lowering of the freezing-point of water than the remaining alkali nitrates; and it will be shown later by data now in hand, that the nitrates of the alkaline earths, with a greater number of molecules of water of crystallization, give still greater freezing-point lowering.

If we turn to Fig. 5, we see that sodium sulphate has water of crystallization, but the quantity depends on the conditions, and all of its water is held in very unstable equilibrium. The same remarks apply to sodium carbonate in Fig. 6.

A large number of similar relations will be pointed out in our next paper in the *American Chemical Journal*, April, 1904, and we have found many other relations of a similar character brought out by data now in hand, and which will be published in a few months.

All in all, the relations are so clean cut and unambiguous that we now do not hesitate to accept the conclusion *that hydrates exist in concentrated solutions of electrolytes.*

We have gone farther and *calculated the composition of such hydrates* for a number of substances, and the change in the composition of the hydrates of a given substance with change in the dilution of the solution.

These results were plotted as curves and will soon be published.[1] The curves expressing the relation between the composition of the hydrates and the concentration of the solutions, came out surprisingly smooth when we consider that every point on the curve contains no less than four experimentally determined values.

All things considered, then, the view which explains very satisfactorily our results is that originally suggested by Jones and Chambers, viz., that in the concentrated solutions there is combination between the molecules of the dissolved substance and the molecules of the solvent, thus removing a part of the solvent, as far as freezing-point lowering is concerned.

To explain the conductivity result it is also necessary to assume that there is a certain amount of electrolytic dissociation, together with the hydration, existing in these solutions.

We are extending this investigation to solvents other than water, to see whether a similar phenomenon manifests itself with non-aqueous solvents, and shall also study a much larger number of electrolytes in aqueous solution.

Chemical Laboratory, Johns Hopkins University,
November, 1903.

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[1] Amer. Chem. Jour., April, 1904.

A METHOD FOR THE DETERMINATION OF COEFFICIENTS OF MUTUAL INDUCTION.

By A. Trowbridge.

THE principal methods for the determination of coefficients of mutual induction fall into three groups:

1. By comparison with self induction (which may be separately determined in absolute measure).[1]
2. By comparison with electrostatic capacity.[2]
3. By comparison with ohmic resistance.[3]

The first two are zero methods — the third is not, as it involves the use of a ballistic galvanometer.

For some time past I have been using a method in the laboratory which falls into group 1 and which has proved so satisfactory both as regards accuracy and simplicity that I publish it, thinking it may, for these reasons, commend itself. The very simplicity of the method made me at first suspect that it must have been adopted by others but on going over the literature of the subject as thoroughly as I am able, I find no description of the method.

Two coils of mutual inductance M and of self-inductances L_1 and L_2 when joined in series with the windings in the same direction are equivalant to a single coil of self-inductance equal to the sum of the coefficients of self-induction increased by twice the coefficient of mutual induction.

When the coils are joined in series so that the lines of force from one oppose the lines from the others, the system is equivalent to a single self-inductance equal to the sum of the coefficients of self-induction diminished by twice the coefficient of mutual induction.

The two coils (provided with a commutator for reversing the direction of the current through one of them) may be put in one branch of a Wheatstone bridge, the other branches of which consist of two noninductive resistances and a variable standard of self-induction.

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[1] See Maxwell, "Electricity and Magnetism," Vol. II., 365, or Carhart and Patterson, "Electrical Measurements," p. 272.

[2] See Carey-Foster, Phil. Mag., 23, 121.

[3] See Glazebrook, Phil. Trans., 1883.

A balance for steady currents and for variable currents being obtained when the currents are in the same direction through the two coils gives $L' = L_1 + 2M + L_2$.

Repeating the balancing when the currents are in opposite directions through the two coils gives $L'' = L_1 - 2M + L_2$.

Combining these expressions gives $L' - L'' = 4M$ or $M = \frac{1}{4}(L' - L'')$. Thus M is got simply from the difference in the settings of the variable standard of self-induction in the two cases.

If such a standard is not available the determination of M becomes more tedious and may be effected as follows: A coil of self-inductance L may be prepared and used as a substitute for the variable standard mentioned above. It is well to choose the value of L about intermediate between L' and L''.

By the bridge method the ratios of L' to L and of L'' to L may be found — calling these p and q, respectively, the expression $M = 1/4\ (L' - L'')$ becomes $M = L/4\ (p - q)$.

If L be determined by balancing against electrostatic capacity then M may be calculated since p and q are numerical expressions obtained by the use of the bridge.

In the following table are given the results of a series of observations to determine the coefficients of mutual induction of a certian pair of coils. Those obtained with the aid of a variable standard are given in column I. Those obtained in the manner just described are given in the second column.

As a basis of comparison of the results obtainable by the method of reversing the coils with those obtainable by the same observer using some of the standard methods the coefficient of the coils was determined by the Maxwell method (group 1), by the Carey-Foster Method (group 2) and by the Glazebrook method (group 3).

The results are given in the third, fourth and fifth columns of the tables. The departures of the individual observations from the mean are also shown in each case.

The mutual induction consisted two similar circular brass frames 93.3 mm. in diameter, the annular region in which the wire was wound being 56.7 mm. in the plane of the windings and 22 mm. at right angles to it.

Each coil consisted of 23 turns per layer and 20 layers of No. 20 copper wire.

The resistance and self-inductance of each coil were respectively, 6.40 ohms and 0.0330 Henry.

All necessary precautions were taken to prevent the disturbing effects of thermal electromotive forces and of direct magnetic action of the coils on the galvanometer. The results given in the first four columns of the table were obtained by the use of a Thomson astatic galvanometer of 1070 ohms resistance and of sensibility of the order of 10^{-9} amperes.

The results shown in the last column were obtained by the use of a Nalder pattern ballistic galvanometer of 2400 ohms resistance of high sensibility adjusted to a period of about 5 seconds.

Table of determinations of M in Henrys by the various methods.

	I.	II.	III.	IV.	V.
	0.01535	0.01560	0.01567	0.01547	0.01528
	0.01545	0.01530	0.01564	0.01568	0.01504
	0.01540	0.01530	0.01542	0.01590	0.01499
	0.01535	0.01507	0.01510	0.01545	0.01528
	0.01548	0.01570	0.01564	0.01490	0.01470
Average,	0.01540	0.01539	0.01549	0.01548	0.01506

Table of departures of individual values from the mean.

	I.	II.	III.	IV.	V.
	−0.00005	+0.00021	+0.00018	−0.00001	+0.00022
	+0.00005	−0.00009	+0.00015	+0.00020	−0.00002
	±0.00000	−0.00009	−0.00007	+0.00042	−0.00007
	−0.00005	−0.00013	−0.00039	−0.00003	+0.00022
	+0.00008	+0.00031	+0.00015	−0.00050	−0.00036
Average,	0.00005	0.00021	0.00019	0.00023	0.00018

I am indebted to Miss Georgiana M. Whitcomb for her very conscientious work in obtaining the data contained in the table.

It appears that with the ordinary appliances of a laboratory equipped for advanced electrical measurements the first method is the most accurate, while the others show about an equal accuracy.

As regards the time required to perform the experiment, the first method has a very decided advantage.

PHYSICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN,
November, 1903.

THE THEORY OF THE COMPOUND PENDULUM: CORRECTION.

By Robert R. Tatnall.

IN my paper on the Theory of the Compound Pendulum, in the Physical Review for December, 1903, I desire to correct an error, pointed out by my friend Lloyd Balderston, Jr., of the University of Pennsylvania.

After indicating the existence of a minimum period for a certain position of the sliding bob, between the centers of suspension and oscillation, I have, on p. 461, interpreted this fact to mean that a particle added below this minimum point would shorten the period, while a particle added higher up would lengthen the period. This is a mistake, since a particle added anywhere between the centers of suspension and oscillation will shorten the period, though the effect diminishes as the point of attachment approaches either of these centers, but nowhere changes sign within these limits. The same error appears again on p. 463, where it is implied that the example quoted from Routh is inconsistent with the fact of minimum period. There is, of course, no such inconsistency. The insertion of the two paragraphs concerned was entirely gratuitous, and the error thus introduced in no way affects the main argument of the paper, or the experimental evidence upon which it is established.

Mr. L. B. Tuckerman, Jr., of Ohio State University, has kindly pointed out that no imaginary values of x can occur in equation (5).

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

ON THE CHARACTER OF THE RADIATION FROM ORDINARY METALS.[1]

By E. F. Burton, B.A.

EXPERIMENTS made by a number of investigators[2] have shown that the conductivity of a mass of air confined in a closed metallic vessel depends upon the nature of the material of which the walls of the vessel are made. Patterson included in his experiments in this connection the determination of the conductivity of air at different pressures and found but little variation when using a small sheet-iron cylinder as the containing vessel when the pressure was reduced from one to about one third of an atmosphere; below a pressure of one third of an atmosphere he found the conductivity approximately proportional to the density of the air. From his results he deduced the conclusion that the conductivity of the confined air was probably due to the existence of an easily absorbed radiation from the walls of the receiver. In the conjoint paper by Professor McLennan and myself the results of a set of observations are given which fail to confirm the conclusions of Patterson. In our investigation it was found that the conductivity of ordinary air enclosed in a large galvanized-iron cylinder varied directly as the density over a range of pressures extending from 500 to 5 cm. of mercury. From this result we were led to conclude that the conductivity of the enclosed air was in a great measure due to a radiation not easily absorbed. Further experiments showed that part of this penetrating radiation, at least,

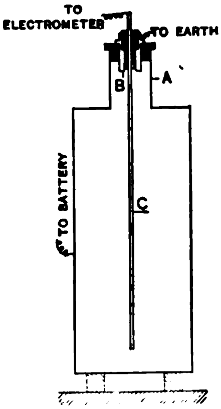

Fig. 1.

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[1] Abstract of a paper presented at the meeting of the Physical Society held on December 30, 1903.

[2] McLennan and Burton, American Physical Society, Dec., 1902. Patterson, Proc. Camb. Phil. Soc., XII., p. 44. Strutt, Nature, Feb. 19, 1903.

had its source outside of the cylinder — a result confirmed by the experiments of Rutherford and Cook.[1]

The object of the experiments described in the present paper was to cut off entirely, if possible, this penetrating radiation from an external source and to determine the nature of the remaining radiation from the walls of the containing vessel.

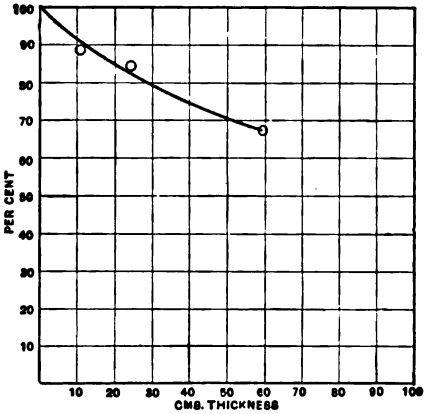

Fig. 2.

The apparatus used was similar to that adopted in the experiment, referred to above. The air was enclosed in a cylinder of galvanized irons 125 cm. long and 30 cm. in diameter, such as that shown in Fig. 1. Into a tube *A*, about 20 cm. long, fastened into the top of the cylinder was fitted an ebonite plug about 5 cm. in diameter. A brass tube *B* was passed through this and into *B* a second ebonite plug was tightly fitted. The second plug carried a brass rod *C* which extended almost to the bottom of the cylinder. The brass tube *B*, which was earthed throughout the measurements, served as a guard tube and prevented any leak from the cylinder to the rod *C* across the ebonite plugs. The rod *C* was connected to a sensitive electrometer and the cylinder was kept charged to about 240 volts. The conductivity was measured by determining the saturation current through the enclosed air to the brass rod. In the attempts to cut off the external radiation the cylinder was immersed successively in water contained in tanks of different sizes, the whole being carefully insulated.

Tanks of three sizes were employed so as to give screens of water of thickness 10.5 cm., 24 cm., and 60 cm. respectively. The decrease in the conductivity in each case is shown in Table I.

---

[1] Rutherford and Cook, American Physical Society, Dec., 1902. Cook, Phil. Mag., Oct., 1903, p. 403.

Table I.

Thickness of Screen of Water.	Decrease in Conductivity.
10.5 cm.	11.9 per cent.
24	15.4 "
60	32.4 "

These values, which are approximately proportional to the thickness of the water layers surrounding the cylinder, are exhibited by the curve in Fig. 2, which shows that a water envelope of considerably greater thickness than 60 cm. would be required in order to cut off completely the penetrating radiation. As apparatus suitable for this purpose was not available, the experiments with water screens were not carried further.

Table II.

Pressure in mm.	Current — Arbitrary Scale.	Pressure in mm.	Current — Arbitrary Scale.
752	20.8	238	10.6
652	19.84	142	6.8
548	18.3	49	2.7
444	15.8	19	1.36
347	14.9		

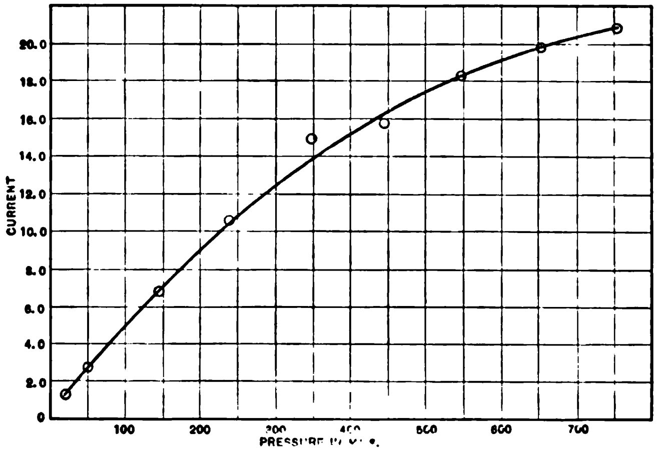

Fig. 3.

While the cylinder was immersed in the largest tank the pressure was reduced from 752 mm. of mercury to 19 mm. and the conductivity measured at various pressures. The values given in Table II. and represented graphically in Fig. 3 show that again the conductivity is almost exactly proportional to the pressure and that, therefore, the remaining conductivity was due rather to a penetrating radiation than to one easily absorbed.

My most sincere thanks are due to Professor McLennan, under whose kind supervision the work was carried out.

NEW BOOKS.

Light for Students. BY EDWIN EDSER. London, Macmillan, 1902. Pp. 574, 12.

This book has been written, according to the author's own statement in the preface, to meet the requirements of students who wish to obtain an accurate and comprehensive knowledge of geometrical and physical optics. The mathematical investigations have been rendered as simple as possible, the desire being to direct the attention to the physical aspect of the subject. The first 218 pages are devoted to the presentation of geometrical optics and the theory of optical instruments. The treatment of this branch of the science is clear, simple, complete, and in every way satisfactory.

The remaining 356 pages treat of the physical optics. In this portion of the book the author has included full explanations of many points not usually dealt with in works of similar scope, such as the investigation of the velocity of transverse waves in an elastic solid, and Sellmeier's theory of dispersion. He has however, found it impossible to include any mention of the electromagnetic theory. Although the electromagnetic theory is not discussed, electrons are introduced as the source of light waves on page 337; and, on page 348, we are told that "electric waves appear to be exactly similar to the waves producing ultraviolet, visible, and infra-red spectra." Also the mechanical pressure of light, which does not exist in the elastic solid theory of light, receives an interesting and satisfactory presentation on page 361.

Viewed, however, from the author's standpoint, namely that of imparting accurate knowledge, the value of the book is great, since it is a veritable storehouse of accurate and modern information. Hence it is indispensible as a book of reference, to the physicist and optician. We must however confess that we think its field of usefulness would have been much wider if more attention had been given to the imaginative side of the subject.

On page 457, the numerical value of the resolving power is given as only half as great as it should be, *i. e.*, it is found to be $Nn/2$ instead of Nn.

C. R. MANN.

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ASTOR, LENOX AND TILDEN FOUNDATIONS.

DOUBLE NUMBER

VOLUME XVIII. NUMBER 4

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY
EDWARD L. NICHOLS
ERNEST MERRITT, and FREDERICK BEDELL

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THE

PHYSICAL REVIEW.

THE METALLIC REFLECTION OF SELENIUM.

By C. K. Edmunds.

Introduction.

1. *Object.*

MUCH recent work has been done on the verification of modern dispersion formulæ as applied to substances having absorption bands in the visible or infra-red regions of the spectrum. Very little has been done on substances possessing absorption bands beginning in the visible region and extending out into the ultra-violet. Since selenium is a substance of this type the determination of its dispersion curve is of interest.

The dispersion curve for wave-lengths within the absorption band can not be directly determined and recourse must be had to the indirect method of metallic reflection for determining the indices of refraction and absorption in terms of the constants of elliptical polarization, assuming some formula of connection, several of which have been developed by various investigators. This has recently been done most successfully by Pflüger for cyanin, which has a strong absorption in the green. His work shows a very satisfactory verification of the Ketteler-Helmholtz formula for dispersion and Cauchy's formulæ for metallic reflection.

The metallic reflection of selenium is of interest because it is on the border line between transparent and true metallic media, and it is from media occupying such an intermediate position that much is to be learned concerning the true nature of metallic reflection. "Vitreous selenium" reflects blue and violet light metallically and the longer wave-lengths vitreously. By passing it over into the allotropic form known as "metallic selenium," it behaves more like a true metal for all wave-lengths, at least in the visible spectrum.

It is the object of this paper, after briefly recounting the previous work on selenium, to determine just how the reflection from vitreous selenium assumes more and more of the characteristics of true metallic reflection as the wave-length of the incident light is decreased. The phase-condition and azimuth of restored polarization of the reflected light will be studied at various incidences for three different wave-lengths. The changes in these characteristics of the reflection will be noted as the selenium is transformed from the vitreous to the metallic form. The data thus secured will be interpreted analytically in order to secure values of the indices of refraction and absorption to compare with those determined directly by other workers.

The improvements in the methods of spectrophotometry in recent years have given a very satisfactory way of testing the formulæ for the reflecting power of media whose indices of refraction and absorption are known. Murphy[1] in 1897 verified Fresnel's reflection formulæ for glass as a type of transparent media, but so far as I know, no photometric verification in the case of an absorbing medium, for various angles of incidence and various wave-lengths, has been attempted. It becomes, then, the object of the second part of this paper to verify Cauchy's formulæ (page 203) for the intensity of the light reflected from metallic media, by means of observations with a Brace spectrophotometer.

2. *Forms of Selenium.*

The properties and transformations of the allotropic forms of selenium have been treated recently by Saunders.[2] Three forms are recognized: (1) Liquid (including vitreous, amorphous and soluble selenium); (2) crystalline red, (including perhaps two closely allied forms); (3) crystalline gray or metallic. The vitreous and metallic forms alone are of interest in the present research, and since previous workers have not been uniformly clear as to which form of selenium they employed, or as to the precise treatment of their mirror surfaces, I shall state briefly the general characteristics of these two forms.

---

[1] Murphy, Astro. Phys., Jan. 6, 1-10, 1897.

[2] A. P. Saunders, Jour. Phys. Chem., IV., No. 2, June, 1900, pp. 423-513. A fairly complete bibliography on selenium is included. Some references given in this paper are omitted by Saunders.

The first form has the properties of an ordinary liquid above 220° C.; below this it becomes more and more viscous, remains soft down to about 60°, and at 30°–40° gets quite hard and brittle, showing a red streak. In this form it is called vitreous selenium from its conchoidal and brilliant fracture. Amorphous selenium is the state in which the element separates from solutions of selenious acid on reduction, forming, when dry, an impalpable red powder with no trace of crystallinity. The amorphous form results whenever a deposit is secured from vaporized selenium, and the thin films of selenium secured by cathode deposit are also of the amorphous variety. Finely powdered vitreous selenium cannot be distinguished from the amorphous variety; and conversely, amorphous selenium when warmed to 40°–50° C. darkens in color and coagulates to a soft mass which, on cooling, becomes hard and brittle, assuming somewhat the fracture of the vitreous form.

Gray crystalline or metallic selenium is obtained from any of the other forms at higher temperatures; in presence of certain liquids, the change takes place even at ordinary temperatures. This is the stable form of selenium at all temperatures from ordinary temperatures to the melting point. The other forms are unstable, the red crystalline representing an intermediate stage between "liquid" and metallic selenium. The reverse transformation from metallic into any other form is not possible below 217° C. With lapse of time the vitreous form passes gradually over into the gray crystalline or metallic form. The change in the optical properties accompanying this transition is illustrated by the observations on fresh and old mirrors.

While the preliminary and check observations in this research were made with mirrors of commercial selenium, which is the vitreous modification and contains considerable sulphur and some tellurium as impurities, the mirrors for which the final values are given were made of chemically pure vitreous selenium. Some of the mirrors were converted into the metallic form in a manner described later.

3. *Optical Properties of Selenium. Emission and Absorption Spectra.*

Historical. — The previous work on the optical properties of selenium has comprised observations of the emission and absorption spectra of selenium vapor, the constants of elliptical polarization of light reflected from selenium mirrors, and the determination of its refractive index directly and indirectly. Recently, while this research was under way, Nutting has published values of the reflection coefficient for different wave-lengths.

In 1863 Werther[1] noted the similarity between the spectra of selenium and lead. Ditte[2] (1871) found well-marked yellowish-green lines in the selenium spectrum toward the *E* line, and also two brilliant blue bands near the *G* line. The work of Salet and of Plücker and Hittorf[3] is summarized in the British Association Reports for 1884. The series spectra of selenium, showing principally triplets, was investigated by Runge and Paschen[4] in 1897 and its analogy with the series spectra of oxygen and sulphur was noted.

The absorption spectrum of selenium vapor was studied by Salet (1871) and Gernez (1872), and it was found that white light passed through a porcelain tube containing selenium heated in an atmosphere of dry carbonic anhydride is gradually absorbed from the violet up to the red, without any appearance of black lines; on raising the temperature considerably the spectrum becomes brighter and dark bands appear furrowing the blue and violet.

HISTORICAL ACCOUNT OF THE WORK ON METALLIC REFLECTION OF SELENIUM.

The earliest work on the metallic reflection of selenium, as far as I have found, is that of Jamin[5] (1850), who records the value of the principal incidence, the coefficient of ellipticity and the ratio of amplitudes of the principal incidence, for a single wave-length.

---

[1] Werther, J. pr. Chem., 88, pp. 180–181, 1863.

[2] Ditte, Comp. Rend., 73, p. 622, 1871; Chem. Soc. Jour. (2), 9, p. 1146, 1871.

[3] Brit. Assoc. Rep., 1884, pp. 440, 441.

[4] Runge and Paschen, Wied. Ann. 61, p. 641–686, 1897; also Astro. Phys. Jour., 8, pp. 70–101, 1898.

[5] Jamin, Ann. de Chim. d. Phys., 29, p. 303, 1850.

Quincke (1874) determined the principal incidence and principal azimuth for a number of metals, including selenium, by a modification of Brewster's double mirror method.[1] Though not so stated, his mirrors were in all probability of vitreous selenium. Just before observation they were polished with buckskin and a pinch of jeweler's rouge (p. 342, loc. cit.). Quincke's values of the principal azimuth are much higher than those of other observers, and the dispersion curve deduced from his results by Ketteler[1] gives a steadily *rising* refractive index (n) with increasing wave-length, which is contrary to all other observations, to be discussed presently. Some experiments looking toward a possible explanation of this discrepancy will be mentioned later on.

Glan[2] in 1879 studied the change in phase of monochromatic red light upon reflection from selenium surfaces by the method of Newton's rings for their films. He used vitreous selenium melted between glass plates. His angles of incidence ranged from 18° to 70°, and his results show no great difference for red light between selenium and ordinary transparent substances. He also determined the variation in the difference of phase (Δ) with changing wave-length (λ) (for a given incidence of 30°); his results show only a small change in Δ with change in λ, but Δ increases with decreasing λ, as does the absorption of selenium.

Using a Babinet compensator in the ordinary way Glan measured the phase-difference for selenium in the neigborhood of the principal incidence ($\bar{\varphi}$) and determined $\bar{\varphi}$ by interpolation for wave-lengths $631\mu\mu$ and $508\mu\mu$.

The latest work on the metallic reflection of selenium is that of Cornu[3] (1889) who investigated a portion of the ultra-violet as well as the visible spectrum. In the visible region the phase condition of the reflected light was determined in the usual way with a Bravais compensator.

---

[1] This method is well described and its accuracy shown in a paper by Pflüger on the Metallic Reflection of Solid Cyanin, Wied. Ann., 65, pp. 214–224, 1898.

[2] Ketteler, "Theoretische Optik," Braunschweig, pp. 548–552, 1885.

[3] Glan, Wied. Ann., 7, pp. 650–652, 1879.

[4] Cornu, Comp. Rend., CXIII., 1889, pp. 917–923, 1211.

In the ultra-violet region fluorspar lenses were used and approximate adjustments were made by means of a fluorescent eye-piece the final observations being secured photographically. The difficulty of effecting the double operation of compensator and analyzer was eliminated by using a Jamin-Babinet compensator and noting the displacement of the fringes instead of moving the quartz wedge. The reflected light was focused directly on the face of the compensator, which bore a ruled line for reference ; an image of this, together with that of the displaced fringes, was focused by a second fluorspar lens on a sensitive plate, between which and the compensator was placed the analyzing nicol. Since the position of the fringes is independent of the azimuth of the analyzer, a single exposure would suffice to determine the fringe-displacement, if the analyzer is in position to give the bands at all. The exact azimuth of the reduced polarization was determined by a series of eight or ten exposures on the same plate, the analyzer being rotated each time through a small known angle ; the azimuth for which there was maximum intensity of the fringes is the desired principal azimuth, when the angle of incidence corresponds to a fringe-displacement of $\pi/2$. This method is of course less precise than the measurements in the visible spectrum ; but, so far as I know, this is the only recorded attempt to determine directly the phase relations in metallically reflected ultra-violet light.

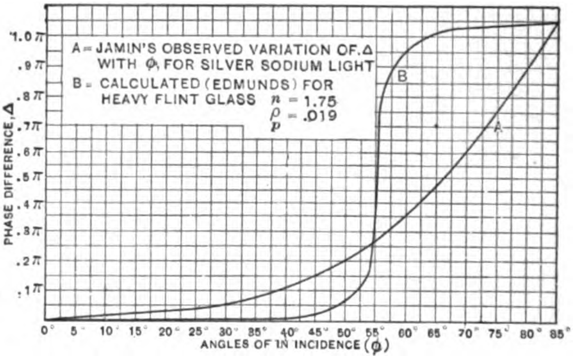

Fig. 1.

Cornu's[1] mirrors were of vitreous selenium melted and pressed out between surfaces of polished quartz. He used two mirrors, one freshly made and the other seven years old. Age gave a more metallic character to the reflection, increasing the absorption very noticeably. Additional evidence along this line was secured in the present research.

---

[1] Cornu, Comp. Rend., LXXXVI., p. 649, 1878.

The results of all previous workers are given in the accompanying table.[1] The wide variation in their observations exhibits the desirability of further work along this line. The work of Glan and of Cornu showed that selenium behaves as a true metal only for the shorter wave-lengths, acting more like a transparent substance for the longer wave-lengths. The difference between the forms of the curves in which the phase-difference (Δ) is plotted as a function of the incidence (φ) for vitreous and for metallic reflection was pointed out by Cornu in 1878, and is shown in the accompanying curves, Fig. 1, for glass and silver. The former shows an inflection at the point $\Delta = \pi/2$ (*i. e.* $\lambda/4$) so that the

TABLE I.

Previous Values of Constants of Elliptical Polarization of Light Reflected from Selenium Surfaces.

λ	$\bar{\phi}$	$\bar{\psi}$	Observer.	References.
	68°10′	10°10′		
280μμ	(64 00)	(11 12)	Cornu.	
431	70 10	15 30	Quincke.	*Jamin:* 1850, Ann. d. Chim. et Phys., Vol. 29, p. 303.
439	71 30	5 00		
439	(68 15)	(7 58)	Cornu.	*Quincke:* 1874, Pogg. Ann., Jubel Bd., p. 336.
486	71 00	13 14	Quincke.	
508	71 28	7 31	Glan.	*Glan:* 1879, Wied. Ann., Vol. 7, p. 640.
527	71 10	12 13	Quincke.	
589	71 23	11 32	Quincke.	
589	68 05	9 55	Jamin.	*Cornu:* 1889, Comptes Rendus, Vol. CVIII., p. 917, 1211.
631	69 49	4 8	Glan.	
656	71 26	8 24	Quincke.	
721	69 35	0 30	Cornu.	
721	(69 00)	(7 00)		

Cornu used two mirrors, one fresh, another seven years old. The figures in parentheses are for the old mirror.

---

[1] Plotted from the results given by Jamin, Ann. de Chim. et d. Phys., 19, p. 315, 1847.

rate of change of phase-difference with respect to the angle of incidence is very large in this region, whereas for metallically reflecting media, the phase-difference rises steadily with increasing incidence, and shows no such inflection. Such a curve showing the connection between the phase difference and the angle of incidence for any one wave-length can not be secured from the observations already cited, and so it was the object of the first part of the present investigation to secure such curves for several wave-lengths which will show just how the reflection from selenium surfaces acquires more or less of a true metallic character as the wave-length of the incident light varies. The general conclusion is that there is no sharp distinction between the two cases of vitreous and metallic reflection, and that selenium, like several other substances such as the aniline dyes, presents the transition from one to the other in a continuous manner as the wave-length of the incident light is changed.

Present Work on the Reflection of Light from Selenium.

Introduction.

The present experimental work on the reflection from selenium surfaces is divided into two main parts in the visible spectrum: (1) The determination of the phase condition and the azimuth of restored polarization of the reflected ray for different angles of incidence for red, yellow and blue light; (2) the direct observation of the reflecting power for various wave-lengths and at different angles of incidence by means of a spectrophotometer.

From a knowledge of the constants of the elliptical polarization of the reflected light as secured from part (1), the values of the refractive index (n) and the absorption coefficient (k') will be secured by an analytical interpretation of the phenomena, and then compared with the directly determined values of k' and n secured by other observers.

The directly observed values of the reflecting power R, secured from part (2) and those of previous workers will be compared with the values calculated from k' and n as given by part (1).

The foundations of the theory of metallic reflection are far from satisfactory physically, and accumulated experimentation under proper and varied conditions is needed for an advance in this direction. The formulæ here used in the reduction of observed quantities to give the optical constants of the medium are not to be regarded as constituting a real theory of metallic reflection, but rather as convenient mathematical aids which, though founded on an unsatisfactory physical basis, have been found to give results which agree well with experiment. A theory of metallic reflection phenomena is yet to be developed in terms of the ionic theory of matter.

Metallic Reflection Formulæ.

Before recounting the present experimental work on the metallic reflection of selenium, attention is called to the formulæ which have been employed throughout the investigation in the reduction or interpretation of experimental results.

Notation.

$n_i \equiv$ index of refraction for incidence i.

$n_0 \equiv$ index of refraction for normal incidence; when written simply n, the variation with incidence is not considered.

$k \equiv$ absorption coefficient as defined by Drude.

$k' \equiv nk$, *i. e.*, absorption coefficient as defined by Walter; see p. 203.

$k_i' \equiv$ absorption coefficient for incidence i.

$k_0' \equiv$ absorption coefficient for incidence 0°, when written simply k', no account is taken of its variation with changing incidence.

$\Delta \equiv \delta_p - \delta_s \equiv$ difference in phase between the two components of the elliptically polarized reflected light, polarized in and normal to the plane of incidence.

$\psi \equiv$ azimuth of "restored" or "reduced" polarization of the reflected light with reference to the plane of incidence.

$\tan \psi = \rho \equiv \frac{A_p}{A_s} =$ ratio of the amplitudes of the two components of the reflected light.

$\varphi \equiv$ angle of incidence.

$\bar{\varphi} = \varphi$ and $\bar{\psi} = \psi$ when $\Delta = \pi/2$, *i. e.*, $\bar{\varphi}$ and $\bar{\psi}$ are the "principal incidence" and "principal azimuth."

$$R \equiv \text{reflecting power} \equiv \frac{\text{intensity of reflected light}}{\text{intensity of incident light}}$$

$$= \frac{A_R^2}{A\varphi^2}, \text{ for normal incidence.}$$

$R_i^p \equiv$ reflecting power at incidence i for light plane polarized in the plane of incidence.

$R_i^s \equiv$ same for light polarized normal to the plane of incidence.

Formulæ.

Approximate.[1]

$$(a)\qquad \begin{cases} k = \sin \Delta \tan 2\psi \\[2ex] n = \sin \varphi \tan \varphi \cdot \dfrac{\cos 2\psi}{1 + \cos \Delta \sin 2\psi} \\[2ex] n^2(1 + k^2) = \sin^2 \varphi \tan^2 \varphi \cdot \dfrac{1 - \cos \Delta \sin 2\psi}{1 + \cos \Delta \sin 2\psi} \end{cases}$$

$$(a')\qquad \begin{cases} k = \tan 2\bar{\psi}, \\ n = \sin \bar{\varphi} \tan \bar{\varphi} \cos 2\bar{\psi} \end{cases} \qquad \text{At principal incidence or } \Delta = \pi/2.$$

More rigorous.[1]

Putting

$$\sin \Delta \tan 2\psi = \tan Q, \quad \cos \Delta \sin 2\psi = \cos P,$$
$$\tan \tfrac{1}{2}P \sin \varphi \tan \varphi = S,$$

and neglecting $1/S^4$ in comparison with 1,

$$(b)\qquad \begin{cases} n = S \cos Q\left(1 + \frac{1}{2}\dfrac{\sin^2 \varphi}{S^2}\right) = S \cos Q(1 + V) \\[2ex] nk \equiv k' = S \sin Q(1 - V), \quad V \equiv \frac{1}{2}\dfrac{\sin^2 \varphi}{S^2} \\[2ex] k = \tan Q\left(\dfrac{1 - V}{1 + V}\right) \text{ or } = \tan Q\left(1 - \dfrac{\sin^2 \varphi}{S^2}\right). \end{cases}$$

(If we further neglect $1/S^2$ in comparison with 1, we get from these last equations those under (*a*) above.)

At principal incidence:

$$\tan \varphi = \tan 2\bar{\psi}, \quad \cos P = 0, \quad S = \sin \bar{\varphi} \tan \bar{\varphi}.$$

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[1] Drude: Theory of Optics, Amer. ed., pp. 274–295, 358–368; Wied. Ann., No. 36, p. 544, 1889; No. 39, p. 507, 1890; No. 64, pp. 161, 162, 1898. See also Winklemann, Handbuch d. Phys., p. 826.

Whence

$$(b')\quad\begin{cases} n = \sin\bar{\varphi}\tan\bar{\varphi}\cos 2\bar{\psi}\left(1 + \dfrac{\cot^2\bar{\varphi}}{2}\right) \\ k' \equiv nk = \sin\bar{\varphi}\tan\bar{\varphi}\sin 2\bar{\psi}\left(1 - \dfrac{\cot^2\bar{\varphi}}{2}\right) \\ k = \tan 2\bar{\psi}(1 - \cot^2\bar{\varphi}). \end{cases}$$

Taking the variation of k' and n with φ into account, Ketteler[1] has deduced the equations of metallic reflection giving n and k' in terms of Δ, φ and φ, which Walter[2] has put in the following form:

More Rigorous Formulæ in a Different Form.

Putting

$$\sin\bar{\varphi}\sin 2\bar{\psi} = \sin\chi,$$

$$\sin 2\bar{\varphi}\sin 2\bar{\psi} = \sin\theta,$$

$$k'_{\bar{\Phi}} = \tan\bar{\varphi}\sin\chi,$$

$$k' \equiv nk.$$

$$n_{\bar{\Phi}} = \tan\bar{\varphi}\cos\chi,$$

$$(c)\quad\begin{cases} k'_{\Phi=0} \equiv k_0' = \tan\bar{\varphi}\sqrt{\sin(\chi + \theta/2)\sin(\chi - \theta/2)}, \\ n_0 = \tan\bar{\varphi}\sqrt{\cos(\chi + \theta/2)\cos(\chi - \theta/2)}. \end{cases}$$

Formulæ for Reflecting Power. (*Cauchy.*)

For normal incidence, *i. e.*, $\varphi = 0$.

Light polarized in any azimuth:

$$(d)\qquad R = \frac{n_0^2(1 + k_0^2) + 1 - 2n_0}{n_0^2(1 + k_0^2) + 1 + 2n_0} = \frac{(n_0 - 1)^2 + k_0'^2}{(n_0 + 1)^2 + k_0'^2},$$

at any angle of incidence $\varphi = i$. For light polarized *in* the plane of incidence,

$$(e)\qquad R_i^p = \frac{\sin^2(i - r_i) + k_i'^2\sin r_i}{\sin^2(i + r_i) + k_i'^2\sin r_i};$$

and for light polarized *normal* to the plane of incidence,

$$(e)\qquad R_i^s = \frac{\cos^2(i + r_i)\tan^2 i + k_i^2\sin^2 r_i}{\cos^2(i - r_i)\tan^2 i + k_i^2\sin^2 r_i}\cdot R_i^p;$$

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[1] Ketteler, Theoretische Optik, Braunschweig, 1885.

[2] Walter, "Die Oberflächen oder Schiller-Farben," Braunschweig, 1895. See also Pflüger, Wied. Ann., LXV., p. 220, 1898.

and $R = \frac{1}{2}(R_i^p + R_i^s)$, for ordinary light.

In these equations $\sin r_i = \dfrac{\sin i}{n_i}$.

$$n_i = \left[\tfrac{1}{2}\left\{\sin^2 i + n_0^2 - k_0^2 + \sqrt{(\sin^2 i - n_0^2 + k_0'^2) + 4n_0^2k_0'^2}\right\}\right]^{\frac{1}{2}}$$

$$k_i' = \left[\tfrac{1}{2}\left\{\sin^2 i - n_0^2 + k_0^2 + \sqrt{(\sin^2 i - n_0^2 + k_0'^2) + 4n_0^2k_0'^2}\right\}\right]^{\frac{1}{2}}$$

or

$$(f)\qquad \begin{cases} n_i = \dfrac{1}{\sqrt{2}}(\sin^2 i + a + b)^{\frac{1}{2}}, \\[2ex] k_i' = \dfrac{1}{\sqrt{2}}(\sin^2 i - a + b)^{\frac{1}{2}}, \end{cases}$$

where $a = n_0^2 - k_0'$ and $b = \{(\sin^2 i - a)^2 - 4n_0^2 k_0'^2\}^{\frac{1}{2}}$.

A very essential difference in notation arises between these formulæ, the failure to notice which has led to errors in some recent papers on metallic reflection. Ketteler and Walter use k to represent the absorption coefficient of the medium in question for a given wave-length of light, regarding it as the damping factor per *wave-length measured in the ether.* On the other hand, Drude uses k to represent the damping factor per wave-length *measured in the medium itself.* The k of Walter is greater than the k of Drude in the ratio of the index of refraction n of the medium, or $k' = nk$, calling k of Walter $\equiv k'$, as is done throughout this paper.

THE CONSTANTS OF METALLIC REFLECTION.

(*a*) *Apparatus and Method of Observation.*

A Meyerstein spectrometer furnished with Nicol's prisms on collimator and telescope (lenses: 25 mm. diameter, 20 cm. focal length, Nicols: 22 mm. x 16 mm. aperture) and with a Jamin-Babinet compensator, was used in the ordinary way to determine the phase difference (Δ) between the two components of the elliptically polarized reflected light in and normal to the plane of incidence, and the azimuth of restored polarization. The shift of the compensator bands was determined with reference to a pair of fixed parallel wires mounted directly on the face of the stationary wedge, and slightly farther apart than the width of a band. The linear scale on the compensator was graduated to .5 mm., and the divided head carried by the screw operating the movable wedge was graduated in 100 parts so that .005 mm. could be measured directly. The distance between two consecutive bands for the shortest wave-length (432 $\mu\mu$) used was 16.78, so that the instrument allowed a difference in phase of .0003 of a wave-length to be measured provided the sharpness of the bands permited so close a setting. As a matter of fact the error in setting on the bands was such that the mean of ten readings is sure only to about .001 λ. Ten settings were made on each band with the screw always moving right-handedly. The variation from the mean is less than 1 per cent. and the variation in the determinations of the distances between consecutive bands is about 0.3 per cent. Settings were made on the bands with the analyzer in each of the conjugate positions, and from three to five bands were observed in each case in order to eliminate any variations in the figure of the wedges. A preliminary test of the wedge and a calibration of the screw proved the combination to be reliable to within the range of error of setting on a band.

In the azimuth determinations twenty settings of the analyzer were made for each of the conjugate positions, making forty settings in all for the full determination of an azimuth. Ten readings were taken in each quadrant in order to eliminate any eccentricity of the nicol in its mounting and also any local errors of graduation on the circular head, which could be read by a vernier to 1′ of arc. Successive settings for maximum sharpness of the compensator bands varied by about three degrees, generally less, and the probable error in the azimuth determination, so far as the purely instrumental errors are concerned, is about 25′.[2]

The position of the central table carrying the mirror could be read directly to 1′ and the position of this table when the mirror was normal to the collimator could be determined by successive trials to within 2′. The angle of incidence is then accurate to be about this amount. The telescope was brought into the proper position by means of a vertical hair in the eye-piece which was brought to the center of the reflected image of the collimator slit

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[1] See Drude, Theory of Optics, pp. 255–258; or Preston, Theory of Light, pp. 404–409.

[2] The effect of a poor mirror surface on the value of the azimuth is noted later on.

for each new angle of incidence, and was then focused on the compensator. Since both the bands and the reference wires are outside the telescope, changing the focus back and forth from the collimator slit to the face of the compensator introduced no error.

The source of light for the red and blue was a Nernst filament (110 volts) the radiation from which was focused on the collimator slit after passing through appropriate screens to render it monochromatic. A plate of dense cobalt glass combined with a potassium bichromate screen gave a bright nearly monochromatic band of red light, and in the blue a double thickness of cobalt glass combined with a thin sheet of "signal green" gave a fairly monochromatic band. The wave-lengths transmitted by these screens were determined by locating the maximum intensity of the light transmitted by them when placed before the slit of an auxiliary prism-spectrometer, the horizontal surface of which had been previously calibrated in terms of known Fraunhofer lines. These wave-lengths were 735 $\mu\mu$ and 432 $\mu\mu$ respectively. For the yellow, a sodium flame was, used. The correctness of the wave-length determinations is tested by their agreement with the distances between consecutive compensator bands for the three different colors.

	Red. Sc. Divs.	Yellow.	Blue.
Distance between bands.	28.56	22.86	16.78
Wave lengths.	735 $\mu\mu$.	589 $\mu\mu$.	432 $\mu\mu$.
Ratio.	.03885	.03881	.03861

(*b*) *Method of Making Mirrors.*

(*b_1*) *Vitreous Selenium.* — To give accurate results the mirror surfaces must be free from scratches, free from films of any foreign substances, and must be perfectly plane; the latter is a rigorous requirement only in measurements of the absolute reflecting power.

In order to secure as clean mirrors as possible, the selenium was melted in a small porcelain crucible and a portion of the melted substance from beneath the surface was drawn up by suction into a hot glass tube; from this a bead of molten selenium about 5 mm. in diameter was blown upon a clean warm glass plate and after being pressed out into a circular film some 2 cm. in diameter between this and a second warm glass plate, was allowed to cool under moderate pressure. When cold, one of the glass plates was knocked off. From a large number of mirrors thus made, the best were selected.

The glass covers were of the plane parallel "crystal" plate, selected for freedom from scratches. They were thoroughly cleaned, and just before being warmed to receive the bead of molten selenium, they were wiped with clean cotton wool dampened with alcohol and then wiped dry. With these precautions and using c. p. selenium, good mirror surfaces could be secured, without polishing, of about two to five square centimeters area. Any small regions which seemed defective were covered with black paper, as were also all exposed parts of the glass backing.[1] When not actually in use, the mirrors were wrapped in clean tissue paper. These details are given because the treatment and condition of the mirror surfaces are of prime importance on account of the rôle which the so-called "surface-layer" plays in metallic reflection.

(b_2) *Metallic Selenium.* — Some of the films of vitreous selenium thus formed were converted before the glass plate was removed into the metallic or gray crystalline variety by being heated in an oven at about 180° C. for 4–6 hours, and then allowed to cool gradually. When cold they no longer adhered to the glass covers and were very brittle; their surfaces were far from mirror-like, showing a dull gray luster. To secure a mirror such a film was cemented to a glass plate and the exposed surface thoroughly polished with soft chamois skin and jeweler's rouge, and just before observation they were rubbed slightly with clean chamois. An attempt was made to get a better surface before polishing with the rouge by rubbing the metallic film with fine "crocus" cloth, but the selenium scratched too readily. The mirrors of metallic selenium were not so perfect as the vitreous ones, and the numerical values given for them later on are to be regarded merely as indicating the direction of the modification in the reflected light, not the exact magnitude of the change.

The effect of polishing a mirror of vitreous selenium was also tried in order to correlate, if possible, Quincke's values for polished mirrors with Cornu's and my own for unpolished vitreous mirrors.

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[1] Cf. Drude, Wied. Ann., 39, p. 497, 1890.

TABLE II.

Kind of Mirror: Vitreous Selenium, Unpolished.

	Wave-Length: 735μμ. Distance Between Bands: 2a = 28.56 Sc. Div.				589μμ 22.86.				439μμ 16.78.			
ϕ	Shift δx	Phase Δ in π	ψ	Ratio of Amplitudes A_p/A_s	δx	Δ	ψ	A_p/A_s	δx	Δ	ψ	A_p/A_s
20°			41°21′	.880	0.60	.0525	42°08′	.905	0.38	.0453	42°03′	.902
30	0.32	.0224					40 36	.857				
40			32 14	.630	1.60	.1400	34 09	.678	0.61	.0727	32 19	.633
50							27 15	.515				
60	0.87	.0610	16 51	.303	2.30	.2012	18 25	.333	1.18	.1405	23 53	.443
65	1.32	.0926	10 24	.184	2.98	.2607	13 30	.240	1.88	.2241	13 36	.242
67			8 50	.155								
68	3.72	.2609	7 45	.136	3.40	.2974	11 42	.207	2.42	.2884	11 33	.204
69												
70	6.88	.4825	6 17	.110	4.52	.3954	9 03	.159	3.14	.3742	10 09	.179
71												
72												
73	10.91	.7651	8 14	.145	7.64	.6684	9 34	.168	4.76	.5673	10 55	
75	12.54	.8794	11 33	.204	8.66	.7576	10 35	.187	5.31	.6329	12 00	.213
78	13.11	.9194	16 55	.304								
80	13.48	.9453	22 35	.416	10.46	.9151	19 43	.358	6.90	.8224	17 43	.320

Notation: δx = mean shift of bands with reference to their position for direct transmission. $\Delta = \delta_p - \delta_s = \frac{\delta x}{a}\pi$ where a = half distance between consecutive bands. $\psi = \frac{\psi'' - \psi'}{2}$ where ψ'' and ψ' are the mean settings of the analyzer for the two sets of bands.

$$\frac{A_p}{A_s} = \frac{\text{amplitude} \parallel \text{to incidence-plane}}{\text{amplitude} \perp \text{to incidence-plane}} = \tan \psi.$$

(*e*) *Results.*

(*c_1*) *General Transition from Vitreous to Metallic Reflection with Decreasing Wave-length.* — The observed values of the phase-difference (Δ) and the azimuth (ψ) for various angles of incidence for different wave-lengths and for the several kinds of mirrors are given in the following tables (II.–IV.) and are also represented graphically in the accompanying curves.

The quantities observed for each incidence are: (1) The settings of the analyzer for maximum sharpness of the two sets of compensator bands, from which the azimuth is secured by the relation $\psi = \frac{1}{2}(\psi'' - \psi')$; (2) the position of the bands in each case, from which, by reference to their positions for direct transmission, δx can be determined, and so Δ by the relation $\Delta = \pi\delta x/a$, where a is the half-distance between consecutive bands. The ratio of amplitudes A_p/A_s is given by the relation $A_p/A_s = \tan\psi$.

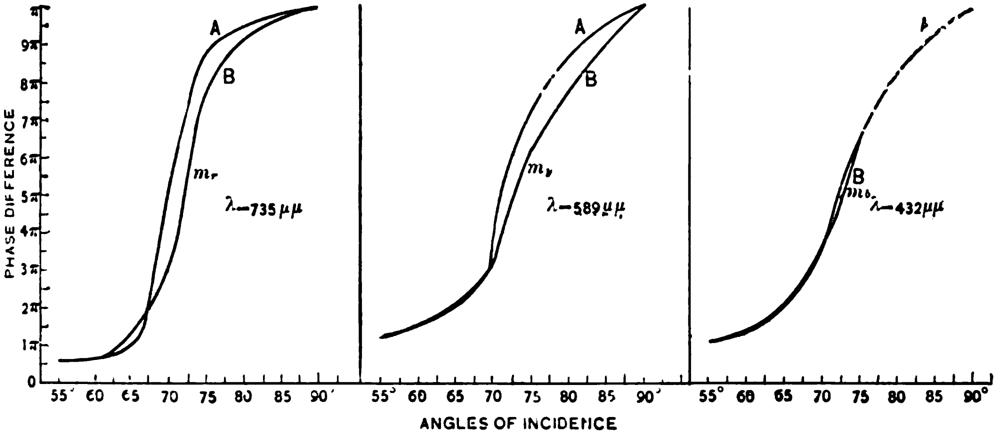

Fig. 2. Difference in the phase conditions of light reflected from mirrors of vitreous and metallic selenium. Curves *A* are for vitreous selenium. Curves *B* are for metallic selenium.

Table II. is for an unpolished mirror of vitreous selenium. The variation of phase-difference and of amplitude-ratio with change of incidence is shown by the curves in Figs. 2, 3 and 5, from which it is seen by comparison with those of Fig. 1 for glass and for silver, that selenium behaves in the matter of elliptical polarization by reflection more like a transparent substance for the longer wave-lengths, and more metallically for the shorter wave-lengths. The gradual disappearance of the region of inflection near $J = \pi/2$ as we pass from red to blue is well brought out in the phase curves, as is also the disappearance of the sharpness of the minimum in A_p/A_s in the amplitude curves.

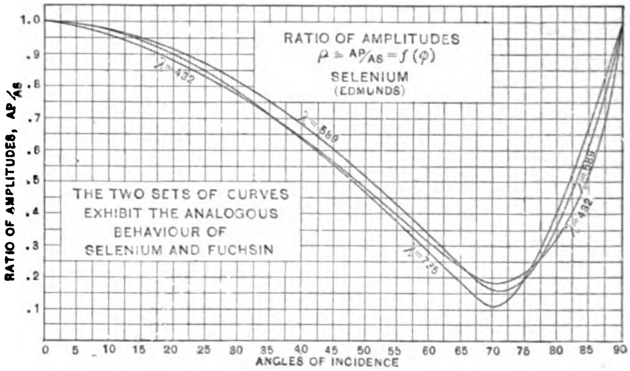

Fig. 3.

Similar curves secured by Merkel for fuchsin, Figs. 4 and 6, are presented for comparison with those of selenium. The change in the character of the phase curves and of the amplitude curves, as we pass from longer to shorter wave-lengths, is perfectly analogous in the two cases, though, of course, for fuchsin the amount or rapidity of the transition is much more marked than for selenium.

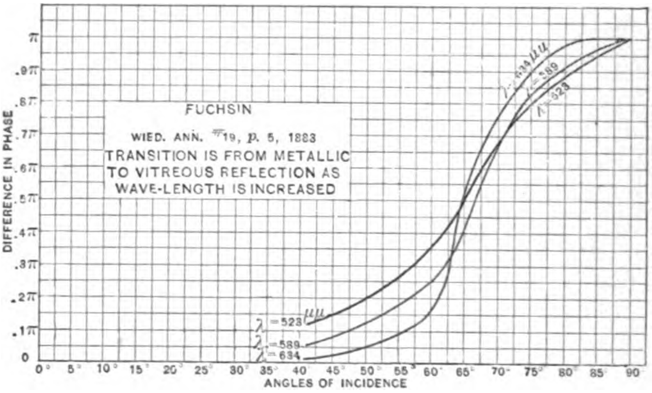

Fig. 4.

This gradual disappearance of the region of inflection in the phase curves and the broadening or rounding off of the minimum in the amplitude curves is characteristic of substances possessing surface color, and the magnitude of the transition as different wave-lengths are used determines the prominence or intensity of the surface color. I shall discuss the surface color of selenium in more detail later in the paper.

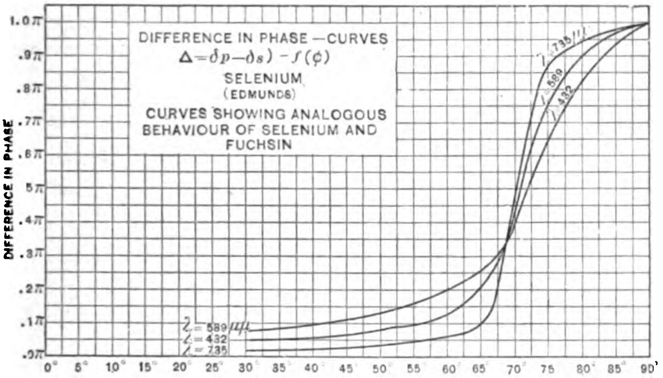

Fig. 5.

Curves *A* and *B* in Fig. 1 represent the two limiting cases of elliptical polarization by reflection; the first is characteristic for very heavily absorbing media, and the latter for perfectly transparent media. The equations which can be deduced on the electromagnetic theory for a relation between the difference in phase

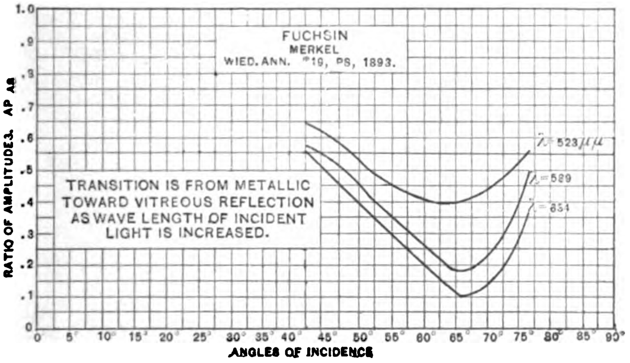

Fig. 6.

and the angle of incidence in terms of the optical constants of the medium apply perfectly well to these limiting cases. But in the case of a medium which is neither transparent nor very heavily absorbing, such as selenium or fuchsin for certain wave-lengths, notably the red, some ambiguity may arise as to which set of equations to apply, *i. e.*, under which method of interpretation shall the experimental results be treated, for the experimental curves themselves lie between the two characteristic curves *A* and *B*. An examination of the analytical development by which the final relations between φ, Δ, ψ, k' and n are obtained in the case of true metallic reflection seems to show that there is no objection to applying them to any case where k' has a value, no matter if small; and this has been done by Pflüger[1] and others in deducing k' and n from observed values of the principal incidence $\bar{\varphi}$ and the principal azimuth $\bar{\psi}$ in the case of fuchsin and cyanin, the phase curves of which are intermediate between *A* and *B* (Fig. 1) as are the curves for selenium. Ketteler, in giving an analytical interpretation of Quincke's observations on selenium, applied the equations of metallic reflection, but in the case of fuchsin he applied those of vitreous reflection also and presented the comparison of the two methods of interpretation as applied to this latter substance.

This comparison in the case of selenium is presented in the following:

(*a*) Using the experimental curves giving Δ as a function of φ and determining that incidence $\varphi = \bar{\varphi}$ for which $\Delta = \pi/2$, by means of Lagrange's interpolation formula, we get

For $\lambda =$	$735\ \mu\mu$	$589\ \mu\mu$	$432\ \mu\mu$
$\bar{\varphi}_{\Delta=\pi/2} =$	$70^\circ\ 08'$	$71^\circ\ 06'$	$71^\circ\ 34'$
A_p/A_s	.112	.156	.182
$\bar{\psi} = \tan^{-1}_{\Delta=\pi/2}(A_p/A_s)$	$6^\circ\ 23'$	$8^\circ\ 55'$	$10^\circ\ 20'$

These values show an increase in both principal incidence and principal azimuth with decreasing wave-lengths; which is in agreement with the results of Cornu and Glan, but contrary to those of Quincke. The value of $\bar{\varphi}$ determined directly with a quarter-wave plate for sodium light was $\bar{\varphi}_D = 71^\circ\ 32'$, and $\bar{\psi}_D = 9^\circ\ 15'$. Quincke found by the method of double reflection $\bar{\varphi}_D = 71^\circ\ 23'$, but his value of $\bar{\psi}'_D$ is high. I adopt as the final value of φ for $\lambda = 589 \mu\mu$, the mean of my two determinations, viz: $\bar{\psi} = 71° \ 19'$.

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[1] Pflüger, Wied. Ann., 5, 1898, pp. 192–224.

(*b*) Interpreting the experimental curves of vitreous selenium as those of a transparent substance as opposed to a metallically reflecting surface, we can by interpolation determine the angle of maximum polarization, the tangent of which is the index of refraction. We get:

$\lambda =$	$735 \mu\mu$	$589 \mu\mu$	$432 \mu\mu$
ρ_p	.1095	.1509	.1785
φ_p	70° 20′	71° 15′	70° 20′
$n = \tan \varphi_p$	2.798	2.946	2.798

Where $\rho_p \equiv$ minimum value of amplitude-ratio and $\varphi_p \equiv$ corresponding incidence, *i. e.*, the polarizing angle.

This verifies in a general way the turn in the dispersion curve in the green obtained by Professor Wood[1] and Mr. Pfund by means of thin-film interferometer measurements.

(*c*) In the following Table III. values of the phase difference are given for red light, (1) as observed, (2) as calculated on the assumption that selenium acts as a transparent medium, and (3) as calculated on the assumption of true metallic behavior of the selenium for red light. Judging from this table there is hardly any choice as to which set of formulæ to apply to the observations, for the observed values differ as much from one set of calculated values as from the other, and curiously enough in the same direction from both.

A comparison of the values of the refractive index secured by treating selenium as a vitreously reflecting substance with those secured by application of the equations of metallic reflection is presented in accompanying tabulation, which shows that in general the tangent of the polarizing angle gives a higher value of the refractive index than that calculated from the principal incidence and principal azimuth. The difference is greater in the case of fuchsin than for selenium.

A substance for which this transition from vitreous to metallic reflection as different wave-lengths are considered is even more

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[1] Wood, Phil. Mag., June, 1902, p. 607; and also Proc. Phys. Soc. Lond., Vol. XVIII., pp. 607–622, 1902.

TABLE III.

Vitreous Selenium. $\lambda = 735\ \mu\mu$.

Angle of Incidence ϕ.	**Phase Difference. Δ in π.**		
	Observed.	**Cal.**[1]	**Cal.**[2]
30°	.0224	.0142	.0131
60	.0610	.1097	.0932
65	.0926	.1937	.1593
68	.2609	.3192	.2587
70	.4825	.4716	.3964
73	.7651	.7147	.6829
75	.8794	.8100	.8018
78	.9194	.8870	.8886
80	.9453	.9177	.9206

[1] Δ_π calculated on assumption that the selenium acts as a transparent medium for the red, $\phi_p = 70° 19'$, $\rho_p = .1095$; using the formula of Drude given on page 202.

[2] Δ_π calculated on assumption of true metallic behavior by means of Drude's formulæ (Optics, Eng. ed., p. 346; see p. 202, this paper), using $\bar{\phi} = 70° 8'$, $\bar{\psi} = 6° 23'$, whence $k = .1988$, $n = 2.704$.

C: Comparison of Fuchsin and Selenium.

Fuchsin.

λ	455 $\mu\mu$	589 $\mu\mu$	634 $\mu\mu$
Principal incidence, $\bar{\phi}$	48° 00′	67° 00′	64° 00′
Polarizing angle, ϕ_p	44 48	67 15	66 50
Refractive index, n (as cal. from $\bar{\phi}$ and $\bar{\psi}$)	0.687	2.2307	2.0275
$\tan \phi_p$	1.010	2.385	2.337
Principal azimuth, $\bar{\psi}$	26° 50′	9° 40′	5° 15′
Absorption coeff't, k (as cal. from $\bar{\phi}$ and $\bar{\psi}$).	.575	.293	.146
$k' = nk$	.3950	.6534	.2959

Selenium.

λ	432 $\mu\mu$	589 $\mu\mu$	735 $\mu\mu$
$\bar{\phi}$	71° 34′	71° 06′	70° 08′
ϕ_p	70 20	71 15	70 20
n	2.811	2.8198	2.704
$\tan \phi_p$	2.798	2.946	2.798
$\bar{\psi}$	10° 20′	8° 55′	6° 23′
k	.3375	.2863	.1988
$k' = nk$	.9487	.8073	.5375

marked than for selenium or fuchsin, is nitroso-dimethylaniline. Professor Wood has shown that it is transparent to the ultra-violet while having a heavy absorption band in the blue region of the spectrum and another in the extreme ultra-violet, being very transparent for yellow. He locates the center of the first band at 431 $\mu\mu$. Inasmuch as the refractive index cannot for this region be determined by direct prism measurements, I have studied its metallic reflection in a liquid form for $\lambda = 432\,\mu\mu$ in order from a knowledge of the principal incidence and principal azimuth to calculate the indices of absorption and refraction. Suffice it to point out here that for $\lambda = 432\,\mu\mu$ a phase-curve was secured very closely analogous to curve *A* in Fig. 1, while for yellow light, $\lambda = 589\,\mu\mu$, the nitrosodimethylaniline acted very nearly as a neutral liquid giving almost entirely plane polarized light for an incidence of 60° ± ; the region of the minimum on the amplitudes-curve being quite narrow. The results are shown in Fig. 7.

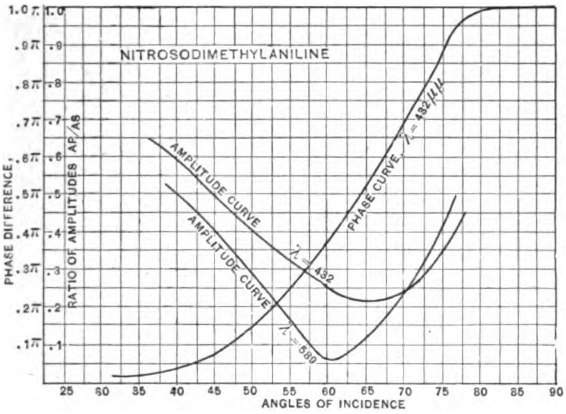

Fig. 7.

This comparison of the methods of interpreting the experimental results suggests that in all probability a result nearer the truth will be secured by applying the formulæ of metallic reflection to the observed values of azimuth and phase difference found for selenium for various incidences. These formulæ are given on page 201, and the result of applying them to the present observations to secure values of absorption coefficient and refractive index are given from here on.

(*d*) Effects of polish and scratches on phase difference (Δ) and azimuth (ψ).

The effect of polishing a mirror of vitreous selenium with chamois skin and rouge is shown in Table IV. There are also recorded for comparison the values of Δ and ψ for $\lambda = 432$ $\mu\mu$ for a mirror which was badly scratched when the glass cover was knocked off in its preparation. The scratches were quite deep and slightly curved. They had a marked effect upon both the azimuth and the difference in phase, giving larger values of the azimuth and smaller values of the phase-difference than for the unpolished mirror. Those parts of the mirror which were not scratched had a much better mirror-surface than many of the other mirrors made. The effect on the phase is in agreement with the results of Drude[2] who showed that scratches on the mirror (made by rubbing it in a single direction with emery cloth No. 0000) in a direction parallel to the plane of incidence had little or no effect on the value of Δ, while scratches perpendicular to the plane of incidence

TABLE IV.

Effects of polish and of scratches on values of Δ and ψ.

Vitreous Selenium.

Kind of Mirror Vitreous Selenium.	$\lambda\mu\mu$	ϕ	ψ	δx	a[1]	Δ	Diff. in Δ
Polished.	589	68°	—	3.46	11.37	$\overset{\pi}{0.3027}$	.0315
Unpolished.	589	68	—	3.10	11.43	0.2712	
Polished.	735	65	13 05	1.87	14.35	0.1303	.0377
Unpolished.	735	65	10 24	1.32	14.26	0.0926	

Diff. in ψ, 241. $\lambda = 432 \mu\mu$.

ϕ	ψ					Δ in π				
	Pol.	Diff.	Unpol.	Diff.	Scrat.	Pol.	Diff.	Unpol.	Diff.	Scrat.
65°	17° 13′	3° 37′	13° 36′	1° 05′	14° 42′	$\overset{\pi}{0.2598}$	$\overset{\pi}{.036}$	$\overset{\pi}{.2241}$	$\overset{\pi}{.002}$	$\overset{\pi}{.226}$
70	12 09	2 00	10 09	3 27	13 36	.4148	.020	.395		
75	13 13	1 13	12 00	3 45	15 45	.6555	.021	.634	.101	.533
80	19 49	2 06	17 43	3 23	21 06	.8700	.046	.824	.016	.808
Approx. Mean dif.		2°+		3°+			+.03π		−.04π	

---

[1] The variations in a are due to the fact that the compensator was removed between these different observations and when replaced did not make the same angle with the light falling on it. But since δx as well as a is affected by the cosine of the angle which the face of compensator makes with the direction of the beam incident on it, the ratio $\delta x/a$, which alone enters the value of Δ, is unaffected.

[2] Drude, Wied. Ann., 39, 1890, pp. 481–554, especially in this connection pp. 497, 498.

gave Δ a little less than the normal value (*i. e.*, the value observed for as perfect mirrors as he could obtain). The difference, however, is small for the metals Drude investigated, amounting only to about $.003\lambda$–$.005\lambda$, while in the present case for vitreous selenium deeply scratched (some of the scratches were also wide), the decrease in phase-difference is $\pi.04$ or $.02\lambda$.

The effect of polishing with rouge and chamois was to increase Δ for all three wave-lengths, the change being slightly greater for the longer wave-lengths, *i. e.*, for those to which the unpolished selenium would be more transparent. This is in accord with previous work of Drude and others on the rôle played by the surface or transition layer, the condition of which is of capital importance in determining the metallic character of the reflection. The surface molecules are altered, perhaps in their manner of aggregation in such a way as to increase the apparent absorption coefficient, and naturally the effect of polishing a pseudo-metal like selenium by increasing the thickness of the transition layer, is more marked for those wave-lengths which before polishing were just on the border line between absorption and transparency.

The effect of polish on the values of the azimuth, ψ, as given by the observations recorded in Table IV., is, in general accord with Drude's results, which showed a larger value of ψ for the better mirror surfaces. The effect of the deep wide scratches in the selenium mirror was to increase ψ some 2° or 3°, and this is in general agreement with Drude's observation that a silver mirror rubbed in a direction normal to the plane of incidence with emery cloth No. 0000 gave ψ somewhat *greater* than for a perfectly good surface. On the other hand, he found that a silver mirror rubbed in all directions with emery cloth gave ψ some 16° *less* than the normal value. The scratches on the selenium mirror were, in general, normal to the plane of incidence, though being slightly curved they were in part somewhat parallel to the plane of incidence.

Scratches parallel to the plane of incidence would naturally be expected to increase the azimuth of the reflected light, since a scratch would reflect a vibration along its length but would have a destroying effect on a vibration at right angles to its length by absorbing it on account of multiple reflections from side to side.

Hence in the light reflected from a scratched mirror there would be a larger relative amount of light whose vibrations were parallel to the orientation of the scratches, and hence the resultant vibration would be turned toward the direction of the scratches and tan $\psi = A_p/A_s$ would be increased and so ψ, the azimuth, would be increased when the scratches are parallel to the plane of incidence.

The opposite would be expected for scratches normal to the plane of incidence.

The true azimuth for an unscratched surface could be secured then, from observations on a scratched mirror by taking the mean of two determinations of ψ made with the mirror in two positions with reference to a horizontal axis (in case the mirror is vertical) which differ by 90.

The values of Δ given in this paper are probably affected by scratches, etc., only within the error of observation, while the values of the azimuth may be a little too small on this account.

(c_{111}) *Metallic Selenium Mirrors.*—Table V. represents the observed values of ψ and Δ for different angles of incidence for a mirror of metallic selenium, made in the manner already described, for red, yellow and blue light. For red, Δ is considerably less for metallic selenium than for a vitreous mirror for all incidences greater than 65°, the same is true for yellow for $\varphi > 68°$ and for blue when $\varphi > 73°$. The effect on the blue is less marked than for yellow and red, and this is what we should expect, inasmuch as the blue is more heavily absorbed by the vitreous form than is either yellow or red, and so the change in Δ made by transforming the mirror from the vitreous to the metallic variety is greater for those wave-lengths for which the vitreous mirror was the more transparent or, rather, less absorbing than the metallic. In general the azimuth of the reflected light is greater for the metallic selenium than for the vitreous, except in the case of red light for $\varphi > 73°$.

The effect *in toto* of the transition from the vitreous to the metallic form is to make the selenium behave more like a true metal for all three wave-lengths investigated, the change being more marked for the longer wave-lengths. This is illustrated in the curves *B*, *B*, *B* in Fig. 2. For blue the change is very slight, indeed, and for red and yellow it is much less than was anticipated by reason of the apparently large difference in the absorption coefficient for red; a film of amorphous selenium 0.1 mm. thick allowing a good deal of red light to pass, while a much thinner film of the metallic variety is entirely opaque.

TABLE V.

Polished Mirror of Metallic Selenium.

ϕ	Wave-Length: 735μμ				589μμ				432μμ			
	Dist. bet. Bands: 16.80 Sc. Divs.				22.76.				28.60.			
	δx	Δ_π	ψ	A_p/A_s	δx	Δ_π	ψ	A_p/A_s	δx	Δ_π	ψ	A_p/A_s
65°	1.84	$^{\pi}$.129	12° 15′	.217	2.38	$^{\pi}$.209	13° 52′	.247	1.86	$^{\pi}$.221	17° 06′	.307
68	3.43	.240	8 15	.145	3.72	.327	11 08	.197	2.43	.290	14 38	.261
70	4.54	.318	7 11	.126	4.10	.360	10 30	.185	3.27	.390	13 22	.237
73	8.62	.603	6 35	.115	6.64	.583	10 45	.190	4.22	.500	13 52	.247
75	11.12	.777	9 57	.175	7.48	.655	12 20	.219	5.42	.645	15 19	.274

REDUCTION OF OBSERVATIONS TO DETERMINE OPTICAL INDICES.

The values of the absorption coefficient (k and k') and the index of refraction (n) secured from the values of the principal incidence ($\bar{\varphi}$) and the principal azimuth ($\bar{\psi}$) observed by previous investigators together with those presented in this paper are given in the following Table VI. Columns 1, 1′ and 1″ have been calculated by the approximate formulæ; 2, 2′ and 2″ by the more rigorous formulæ; 3, 3′ and 3″ by the second form of the more rigorous formulæ. The results show how closely the last two agree, and also how approximate the first really is, giving considerably smaller values of n and larger values of k than the more rigorous formulæ, and of the two latter, the third set of formulæ gives consistently higher values for the absorption while giving identical values of the refractive index in comparison with the second set of formulæ; unless we apply, as I think we should, the formulæ given on page 203 to reduce $n_{\bar{\phi}}$ and $k_{\bar{\phi}}'$ to n_0 and k_0', in which case, as the columns 4 and 3 show, the third set of formulæ gives higher values of the refractive index also.

To secure values of the optical constants which shall agree well with those obtained by direct experiment, the observations of the phase difference and the azimuth must be confined to the immediate neighborhood of the principal incidence, and the second set of

Table VI.

Observed.				Calculated.				Calculated.			Calculated.			
				n				k			$k' = nk$			
Observer.	λ	$\bar{\Phi}$	$\bar{\psi}$	1	2	3	4	1′	2′	3′	1″	2″	3″	4″
Cornu.	280$\mu\mu$	68° 10′	10° 10′	2.172	2.350	2.343	2.333	.3706	.3146	.3186	.8049	.7393	.7465	.6841
" (old).	280	64 00	11 12	1.704	1.906	1.901		.4122	.3246	.3312	.7024	.6187	.6295	
Quincke.	431	70 10	15 30	2.235	2.381	2.381	2.339	.6009	.5275	.5297	1.3430	1.2560	1.2613	1.1757
* Edmunds.	432	71 34	10 20		2.811		2.794		.3375			.9487		.8984
Cornu.	439	71 30	5 00	2.791	2.947	2.944	2.943	.1763	.1576	.1586	.4921	.4644	.4669	.4403
" (old).	439	68 15	7 58	2.239	2.417	2.412		.2855	.2434	.2458	.6392	.5883	.5928	
Quincke.	486	71 00	13 14	2.458	2.604	2.603	2.5956	.4978	.4421	.4439	1.2236	1.1512	1.1554	1.0955
Glan.	508	71 28	7 31	2.731	2.885	2.884	2.863	.2686	.2400	.2439	.7335	.6924	.7033	
Quincke.	527	71 10	12 13	2.526	2.673	2.672	2.649	.4543	.4044	.4062	1.1476	1.0810	1.0855	1.0202
Quincke.	589	71 23	11 32	2.588	2.735	2.733	2.714	.4358	.3801	.3820	1.1279	1.0400	1.0440	.9832
* Edmunds.	589	71 19	8 54		2.8198		2.8076		.2863			.8073		.7637
Glan.	631	69 49	4 8	2.527	2.697	2.692	2.694	.1453	.1269	.1279	.3672	.3422	.3443	.3212
Quincke.	656	71 26	8 24	2.702	2.854	2.851	2.843	.3019	.2697	.2711	.8157	.7697	.7729	.7287
Cornu.	721	69 35	0 30	2.517	2.692	2.686	2.692	.0174	.0152	.0153	.0438	.0409	.0412	.0387
" (old).	721	69 00	7 00	2.360	2.534	2.529		.2493	.2151	.2171	.5883	.5451	.5490	
* Edmunds.	735	70 08	6 23		2.704		2.698		.1988			.5375		.5052

VITREOUS SELENIUM.

Indices of refraction (n_0), *absorption coefficients* (k_0'), *and reflecting power* (R) *calculated from observed values of phase difference* (Δ) *and azimuth* (ψ) *in neighborhood of principal incidence* ($\bar{\phi}$).

	$\lambda = 432\ \mu\mu$				$589\ \mu\mu$			$735\ \mu\mu$		
ϕ	69° 40′	70° 40′	71° 40′	72° 40′	70°	71°	72°	69° 10′	70° 10′	71° 10′
ψ	14° 47′	14° 25′	14° 46′	15° 47′	13° 28′	13° 35′	13° 19′	6° 41′	7° 01′	7° 55′
Δ	$.4592\pi$	$.5371\pi$	$.5849\pi$	$.6244\pi$	$.4747\pi$	$.5444\pi$	$.5927\pi$	$.4300\pi$	$.5333\pi$	$.61695\pi$
log S	.39991	.40540	.40031	.39776	.39625	.41114	.41018	.36850	.40545	.40073
log tan Q	$\bar{1}.75377$	$\bar{1}.73781$	$\bar{1}.73759$	$\bar{1}.75438$	$\bar{1}.70455$	$\bar{1}.70603$	$\bar{1}.68158$	$\bar{1}.36529$	$\bar{1}.39546$	1.42272
n_i	2.3366	2.3852	2.3632	2.3314	2.3796	2.4522	2.4762	2.4579	2.6372	2.6044
k_i	.49332	.47636	.47376	.49080	.4391	.4441	.4189	.1975	.2168	.2297
$n_i k_i = k_i'$	1.1527	1.1365	1.1197	1.1445	1.045	1.089	1.0372	.4855	.5716	.5982
n_0	2.2985	2.3495	2.3271	2.2921	2.3487	2.4214	2.4483	2.4511	2.6296	2.5958
$k_0'(=n_0 k_0)$	1.0733	1.0597	1.0413	1.0621	.9727	1.0176	.9686	.4503	.5356	.5391
	Means (1) $n_0 = 2.3168$		$k_0' = 1.059$		Means (1) $n_0 = 2.406$ $k_0' = .9863$			Means(1) $n_0 = 2.559$ $k_0' = .5150$		
By interpolation using LaGrange's formulæ,										
	$\bar{\phi} = 69° 46'$,		$\bar{\psi} = 14° 43'$		$\bar{\phi} = 70° 22'$, $\bar{\psi} = 13° 31'$			$\bar{\phi} = 69° 50'$, $\bar{\psi} = 6° 54'$		
Whence by Walter's formulæ:										
	(2) $n_0 = 2.3674$		$k_0' = 1.171$		(2) $n_0 = 2.500$ $k_0' = 1.129$			(2) $n_0 = 2.645$ $k_0' = .5716$		
Reflecting power,	$R = 25.50$ % from (2)				$R = 26.06$ % from (2)			$R = 22.28$ % from (2)		
	23.53 " (1)				24.09 " (1)			20.78 " (1)		

formulæ applied. The observations already cited having given for the latter the following values:

$$\lambda = 432\,\mu\mu \qquad 589\,\mu\mu \qquad 735\,\mu\mu.$$
$$\bar{\varphi} = 71^\circ\ 34' \qquad 71^\circ\ 19' \qquad 10^\circ\ 08',$$

observations of phase difference (Δ) and azimuth (ψ) were made on the same mirror (now five months old) as shown by the following summary.

The index of refraction is found to increase with increasing wave-length for an old mirror, and this agrees with Quincke's observations and tends to confirm the view that his mirrors of selenium were not used till some time after making.

Effect of Time on the Principal Incidence and Principal Azimuth. — In order to show the effect of time on the values of the principal incidence ($\bar{\varphi}$) and principal azimuth ($\bar{\psi}$), I shall apply the same method to both mine and Cornu's observations of these constants of elliptical polarization for a fresh and an old mirror. The results are presented in Table VII. Walter's formulæ were used in calculating the index of refraction n_0, the absorption coefficient k_0', and the reflecting power R, from the principal incidence and azimuth.

Lapse of time decreases the principal incidence some 18′ to 1° 48′ after five months interval, the decrease being greater for the shorter wave-lengths. An interval of seven years gave a much larger decrease of from 0° 35′ to 4° 10′ in $\bar{\varphi}$, the greatest change being for the ultra-violet. Interpreted in terms of phase-difference, this means that the surface has changed in such a way as to increase the phase-difference (Δ) for any given incidence and to make the value $\Delta = \pi/2$ occur at a smaller incidence.

The effect of time is to increase the principal azimuth by several degrees in general; no simple variation of this change with wave-length appears and the change after five months is only 31′ for the red. Since, roughly speaking, the absorption is directly proportional to the tan $\bar{\psi}$, the observations show an increase in absorption for all wave-lengths as time elapses.

The effect of these variations in the values of the principal incidence and principal azimuth with time is to decrease the index of refraction and to increase the absorption coefficient, as calculated

TABLE VII.

Effect of Time on Vitreous Selenium.

Observer: Cornu. Time Interval: 7 Years.

Mirror.	$\lambda = 280\mu\mu$					$\lambda = 439\mu\mu$					$\lambda = 721\mu\mu$				
	$\bar{\Phi}$	$\bar{\Psi}$	n_0	k_0	R	$\bar{\Phi}$	$\bar{\Psi}$	n_0	k_0	R	$\bar{\Phi}$	$\bar{\Psi}$	n_0	k_0	R
					%					%					%
New.	68° 10′	10° 10′	2.343	.746	20.08	71° 30′	5° 00′	2.944	.467	25.34	69° 35′	0° 30′	2.686	.041	21.01
Old.	64 00	11 12	1.901	.630	13.71	68 15	7 58	2.412	.593	19.55	69 00	7 00	2.529	.549	19.91
Diffs.	−4 10	+1 02	−0.442	−.116	−6.37	−3 15	+2 58	−0.532	+.126	−5.79	−0 35	+6 30	−.157	+.508	−1.10

Observer: Edmunds. Time Interval: 5 Months.

Mirror.	$\lambda = 432\mu\mu$					$\lambda = 589\mu\mu$					$\lambda = 735\mu\mu$				
	$\bar{\Phi}$	$\bar{\Psi}$	n_0	k_0	R	$\bar{\Phi}$	$\bar{\Psi}$	n_0	k_0	R	$\bar{\Phi}$	$\bar{\Psi}$	n_0	k_0	R
					%					%					%
New.	71° 34′	10° 20′	2.811	.949	27.10	71° 06′	8° 55′	2.820	.807	26.00	70° 08′	6° 23′	2.704	.538	22.79
Old.	69 46	14 43	2.367	1.171	25.50	70 22	13 31	2.500	1.129	26.06	69 50	6 54	2.645	.572	22.28
Diffs.	−1 48	+4 17	−.444	+.232	−1.60	−0 44	+4 36	−.320	+.322	+0.06	−0 18	+0 31	−.069	+.034	+0.51

from these constants of metallic reflection. Both Cornu's observations and mine show the change in the refractive index to be considerable and to be nearly as great after five months as at the end of seven years.

My observations show the absorption coefficient to increase considerably, though less in the red than for yellow and blue; while Cornu's values give a decrease for the ultra-violet and a large increase in the blue and red.

The dispersion and absorption curves obtained by plotting values given in columns 1, 2 and 3 of Table VI. are shown in the accompanying diagram (Fig. 8) together with those directly observed by Sirks and by Wood[1] and Pfund.

The general discrepancy between the results of the several observers is very marked, especially for the absorption coefficient. The difference between the observed values of the principal incidence and principal azimuth of various observers are shown graphically in Fig. 9 and are probably to be accounted for in great part by the influence of scratches, polish, age, etc., as already demonstrated in this paper. The values of the absorption coefficient calculated from these metallic reflection experiments differ as much among themselves as they do from the directly observed values.

COMPARISON OF RESULTS.

In the metallic reflection experiments we are really studying surface conditions only, whereas in the experiments in which direct observations are made for absorption and refraction we are studying phenomena, having their seat inside the medium. In the metallic reflection experiments no doubt the surface conditions have varied widely and in an unknown manner. In the direct measures of absorption, the selenium was in a form entirely different from that employed in the metallic reflection experiments. Wood and Pfund used their films of amorphous selenium secured by cathode deposit, and close examination of these films shows that they are not perfectly continuous but are rather of a spongy structure which accounts in part for the much lower values of absorption secured by these observers, although their neglect to take into account the loss by reflection at the first surface would certainly tend to balance this. Their direct measures of the refractive index, n, were in the red and yellow region of the spectrum made with small-angle prisms of melted vitreous selenium, and as might be expected, there is a closer agreement in that region with the values of *n* calculated from the metallic reflection experiments. In the green-violet region the direct measures of *n* were made by interferometer measurements on very thin films of amorphous selenium, and there is some doubt as to the validity of these results.

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[1] R. W. Wood, Phil. Mag., June, 1902, p. 607.

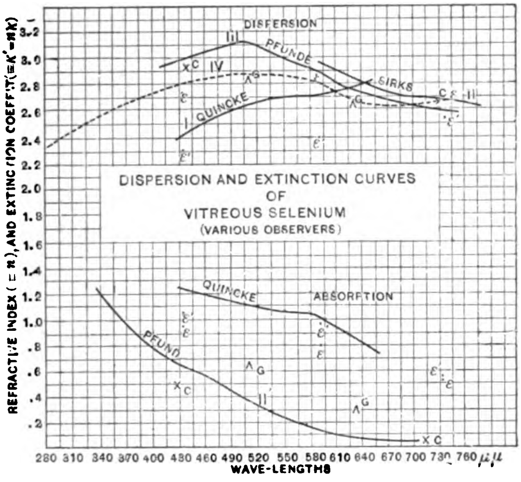

Fig. 8.

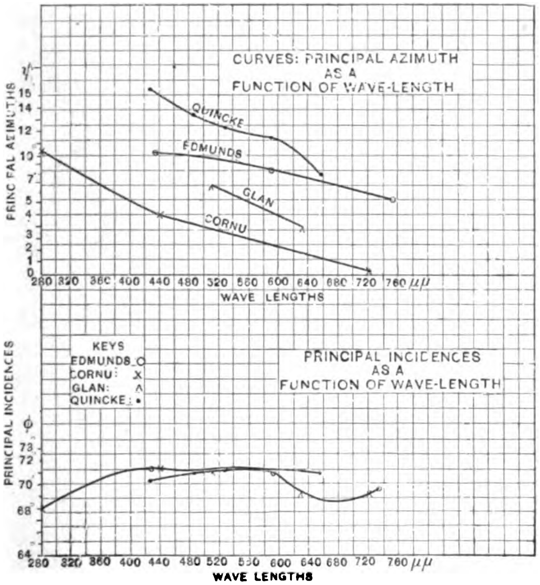

Fig. 9.

Table VIII.

Index of refraction and absorption coefficient of vitreous selenium.

Column:	1	2	3	4	5	6
Wave-Length	n Direct.	Cal. n by Reflec.	kn Direct.	kn Cal. Metal. Reflec.	kn Cal. Reflec.	kn Cal. Reflec.
214$\mu\mu$						
280		2.333		.6841		
334						.9767
395						.9614
400	2.93		.785			
410	2.957					1.0275
415	2.910		.736			
425	2.98		.677			
430						1.1437
431		2.381		1.2613		
432	3.00	2.811		.9487	1.1776	
439		2.947		.4669		
442	3.025		.598		.8205	
454						
466	3.065		.571			
475	3.075					
486		2.604		1.1554		
490	3.120		.478		.4544	
503	3.130					
508		2.885		.7033		
510						1.1354
515			.358			
520	3.085					
524						
527		2.673		1.0855	.7232	
550	3.020		.254			1.0020
580	2.95	2.735		1.0440		
589	2.925	2.8076	.155	0.7637	.7813	.8827
605	2.90					.8415
620					1.1916	1.0728
631		2.697		.3443		
640	2.765		.0879			
656		2.854		.7729	1.1046	
660						
710	2.655		.0456			
721		2.692		.0412		
735		2.704				
748				.5376	.3478	
760	2.61		.0234			

Observers: Cols. 1 and 3, Pfund and Wood.
Cols. 2 and 4, Cornu, Quincke, Glan, Edmunds.
Col. 5, Edmunds.
Col. 6, Nutting (cal. by Edmunds).

From the data at hand, it is extremely uncertain just what form to assign to the dispersion curve of selenium. Quincke's observations, though covering a good portion of the visible spectrum, give, no matter from what point of view we consider them, results which are contrary to those of all other observers. His values of refractive index increase with increase of wave-length, and his values of the absorption coefficient are very much higher than any other determinations. I am at a loss to explain his results except that they may possibly be due, as the high absorption would suggest, to the fact that his mirrors were made some time before he actually observed with them, and so had a chance to pass over into the gray crystalline or metallic form, the apparent absorption of which he further increased by polishing just before observing.

The present work on the metallic reflection of selenium was undertaken to secure merely check values of refractive index and absorption coefficient for two or three wave-lengths in the visible spectrum. It would seem, however, desirable to make a more extended study so as to be able actually to plot a full dispersion curve from a single set of experiments.

Neglecting Quincke's observations, the values of refractive index secured by other determinations of the principal incidence and principal azimuth lie on a smooth dispersion curve which agrees in general "march" with that observed directly. The discrepancy in the values of the absorption coefficient is, however, very great, and further experiments are required to determine the extinction curve of selenium. All that the present observations enable us to say definitely is that the absorption increases from the red toward the blue end of the spectrum. Some experiments attempting to secure "Reststrahlen" in the ultra-violet by multiple reflections from selenium surfaces showed no great increase in reflecting power in that region; if anything, there was a falling off.

Lack of time and a desire to measure the reflecting power of selenium directly by photometric methods have as yet prevented the determination of more accurate dispersion and extinction curves.

The values secured from the present experiments with the fresh mirror for the wave-length $589\mu\mu$ will be used as a basis in calculating the reflecting power for different angles of incidence for comparison with the directly observed values of R. And in determining the absorption curve from the experimentally determined reflection curve for normal incidence, the dispersion curve resulting from all the experiments on metallic reflection, excepting those of Quincke, will be adopted. In this way all the quantities used and compared will result from experiments in which the chief rôle is played by the surface, and so there will be a common ground for the comparison.

SUMMARY OF EXPERIMENTS ON METALLIC REFLECTION.

The present experimental work on the metallic reflection of selenium has shown that the elliptical polarization of plane-polarized light by reflection from vitreous selenium is such as is characteristic of a transparent substance for wave-lengths in the red, and that the reflected light assumes more and more the characteristics of light reflected from true metal surfaces as the wave-length of the incident light is decreased, till in the blue selenium acts quite like a metal. In this respect selenium is somewhat analogous to fuchsin.

The variation of the principal incidence and the principal azimuth with changing wave-length was noted. The principal azimuth increases as the wave-length is decreased, while the principal incidence passes through a minimum at about $680\mu\mu$ and then remains fairly constant as the wave-length is decreased.

The effect of transforming the vitreous selenium into the gray crystalline or metallic form is to increase the absorption for all wave-lengths in the visible spectrum and to render the condition of the elliptically polarized reflected light more like that from a true metal, the change being more marked for yellow light than for blue or red.

Scratches on the surface of the mirror increase the value of the azimuth and decrease the difference in phase of the two components of the reflected light, for any given angle of incidence.

Polishing the mirror with rouge and chamois increases the phase-difference, the change being greater for the wave-lengths to which the unpolished selenium is more transparent. Polishing increases the value of the azimuth for all wave-lengths.

Lapse of time makes the vitreous selenium behave more like a metal, decreasing the principal incidence and increasing the principal azimuth. This is doubtless due to the formation of a surface layer in which the conditions are very different from those of interior portions of the selenium.

The analytical interpretation of the elliptical polarization phenomena by means of formulæ developed chiefly by Drude showed discordant values of the refractive index and absorption coefficient when the observations of different observers are compared. In general, however, the dispersion curve rises as the wave-length is decreased and has a turning point in the green at about $505\mu\mu$. The absorption rises gradually as the wave-length is decreased, and all the experiments as well as the application of the dispersion formulæ seem to indicate a number of overlapping absorption bands in the blue-violet region of the spectrum.

The experiments indicate that the closer and more extended study of the absorption and dispersion of selenium will doubtless present a very interesting case to which as a test the various formulæ of metallic reflection and of the dispersion of metals may be applied.

Johns Hopkins University,
Physical Laboratory, May, 1903.

RESONANCE IN AËRIAL SYSTEMS.

By A. H. Taylor.

THE object of this paper is to outline a simple method of attaining resonance in systems subject to electrical oscillations of high frequency, and to point out several unique lecture-room demonstrations of phenomena peculiar to such systems.

As has been pointed out by Wien (Ann. der Phys., page 686, No. 7, 1902) and others, sharp resonance effects occur only when the damping is small compared to the energy supply. Such an arrangement as is shown in Fig. 1, p. 233, is one to give little damping in the non-radiating, low-resistance circuit, consisting of the condenser, *C*, a spark gap, and the low self-induction, *P*, of the primary of a Tesla coil.

The aërial *A* is coupled magnetically to the system by being connected to the secondary of the Tesla coil *S*, one end of which is earthed. Such an arrangement has been used by Marconi, Braun, Fleming and many others.

The damping of the oscillations in the aërial is very great, but the energy supply from the primary circuit is also great, so that the total damping is small.

The radiation from the aërial depends on the current flowing in it, and this will be a maximum when the natural period of the secondary of the Tesla with its aërial system is the same as the primary period. The secondary period depends on the self-induction of the secondary, of the aërial itself, and upon the capacity of the aërial system relative to earth.

Any measuring device inserted above the secondary *S* is liable to change the relative capacity and hence the period. Even a micrometer spark-gap to measure the potential of the wire to earth will change the capacity of the aërial very materially. The simplest way is to insert a short piece of platinum wire in the earth connection *E*. Being on the earthed side of the system, a Wheatstone's bridge connected to this wire will not change the capacity of the system. The platinum wire may be about 2 cm. of No. 36, and forms one arm of the bridge. The bridge is balanced, and the exciter, a 6″ induction coil used as a step-up transformer, with 10 amperes alternating current at 60 cycles, is turned on. The flow of current in and out of the aërial, and hence in and out of the earth connection, is in nearly all cases large enough to heat the platinum wire and effect a change in resistance of sufficient magnitude to be easily noted with a galvanometer of moderate sensibility, say 10^{-7}.

Then coils of self-inductance are added to the aërial, just above the secondary *S*.

If the galvanometer does not show an increased deflection, hence an increased resistance of the platinum wire, and more current in the aërial, then the capacity of the aërial combined with the self-induction of the secondary *S*, gives a period already slower than that of the primary. In this case a smaller aërial system will have to be used or else the primary period must be lengthened by added capacity or self-inductance in the primary circuit. When once the primary period is slower than that of the secondary and ëarial, added self-induction to the aërial will at first produce a slow increase in the galvanometer deflection, then as syntony is nearly reached, a very rapid increase, attaining a maximum beyond which further addition of self-induction produces a decrease in the deflection. Self-induction is best used in the form of two concentric helices, connected in series so that the mutual induction between the two opposes the self-induction in each. By sliding the inner helix in and out the self-inductance can be smoothly varied, and the resonance point very quickly determined.

The deflections will indicate that the maximum current is often as much as one hundred times as large as the current when the aërial is far out of resonance.

Having the radiating aërial resonating the primary circuit, it is now necessary to have a second primary circuit in tune with the first.

The second Tesla coil should be made with the secondary self-induction as near as possible like that of the first. The primaries should be approximately alike. The second outfit is then tuned to the aërial by adjusting the small variable self-induction p in the primary circuit.

The method is the same as when tuning the aërial to the first primary.

Now we have two oscillators in tune with one aërial, hence, with each other. If they are to stay in tune they must be rigidly mounted, and used in the same relative positions.

The secondary primary may now be removed to the receiving station and a new aërial tuned to it, in which case the two primaries are in tune with each other and with the two aërials. This four-fold resonance is absolutely necessary for the best results.

In case the aërial is coupled, as in Fig. 2, the method is the same, the platinum wire being inserted on the ground side as before. In this case the aërial, with its capacity to earth and inductance, including P, must resonate the impulses in E.M.F. over the induction P considered as part of the primary oscillating circuit.

The case is the same as when a Tesla coil is used, only here we have an auto-transformer coupling of ratio 1 to 1.

The resonance of aërial systems may be very elegantly demonstrated in the lecture room by placing a small lamp, say 1 candle power at 4 volts, either directly in series with the receiving aërial, or across the spark knobs of the primary circuit of the receiver. If an ordinary direct current make and break is used on the coil, the radiated energy attains to high instantaneous values, such as are peculiarly suited to the operation of a coherer or a magnetic detector, but the average energy is far lower than when the alternating current is used, without an interrupter. Hence, to transmit across a lecture room, say a distance of twenty feet, enough energy to light the lamp in the receiving circuit it is necessary to operate the induction coil with alternating current. In this instance a 6″ spark coil carried 15 amperes at 60 cycles and 40 volts. The power factor was at first very low, but as the transmitting aërial came into resonance, the power factor ran as high as 0.5. A spark gap of 2–4 mm. in the primary circuit must, if operated continuously, be cooled by an air-draft to prevent arcing.

This is not ordinarily necessay, as the coil need be run only for short intervals.

In the lecture room the sending aërial may consist of a strip of wire netting about ten feet by two feet, suspended as near the ceiling as possible, and coupled either by the auto-transformer method (Fig. 2) or by the Tesla transformer (Fig. 1) to the sender. The variable self-inductance should be in series with the aërial.

The receiving aërial is similar, and may be used with or without the condenser circuit similar to the primary sender circuit. If the condenser circuit is used, the little lamp is placed across the spark-gap, or rather where the spark-gap would be if the receiver were used as a transmitter. If the circuits have been tuned carefully, the lamp in the receiving circuit will burn brightly and steadily as long as the transmitter operates. If either aërial is thrown out of resonance by varying slightly the self-inductance in series with them, the lamp goes out entirely.

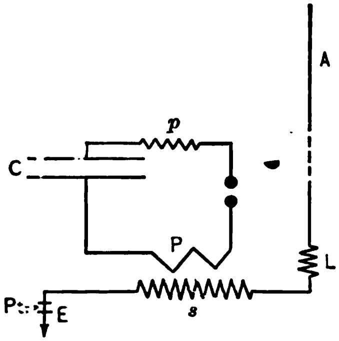

Fig. 1.

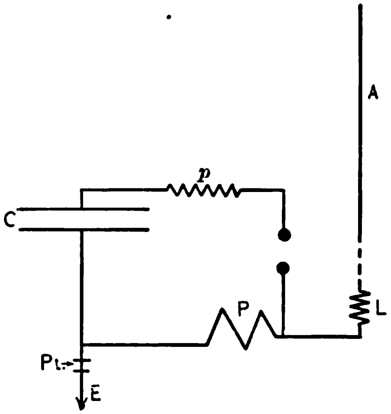

Fig. 2.

If desired, a hot wire voltmeter or ammeter can be used at the spark-gap of the receiving circuit in place of the lamp. Under fair conditions, I have gotten an indication of over an ampere at the receiver, distant 20 feet from the transmitter. This drops to a few tenths of an ampere when either aërial is thrown a little out of resonance. The Tesla coil coupling is best suited for the use of an ammeter, since in the receiver it acts as a step-down transformer. The real current is doubtless somewhat less than that indicated, due to the fact that the ammeter wire has higher resistance with such high frequencies (of the order of 10^6) than it has for ordinary frequencies. The small lamp is better for lecture room demonstrations.

The screening effect of conducting obstacles may be illustrated by interposing a wire netting screen between the two aërials, causing a dimming of the lamps in the receiving circuit. Either aërial may be thrown perceptibly out of tune by a person standing near it, or by holding near it a conductor connected to earth, thereby changing its capacity. A conductor connected to earth may be suspended near the transmitting aerial, and the aërial tuned accordingly to its new capacity by adjusting the variable inductance in series with it. The radiation under these conditions is, however, less than before, as shown by the dimming of the lamp in the receiving circuit. This illustrates the disadvantage of having earthed conductors in the neighborhood of an aërial wire.

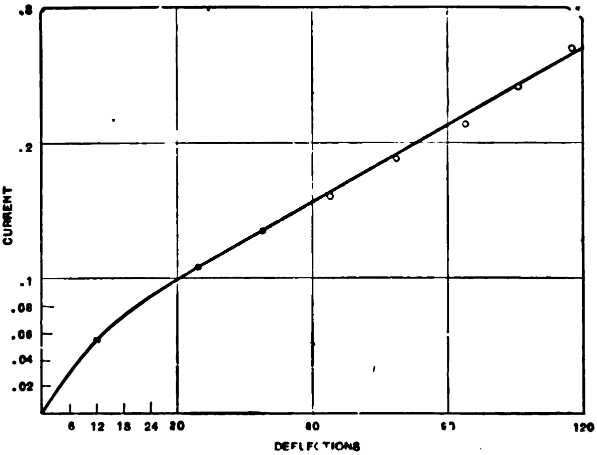

Fig. 3.

In order to plot a resonance curve for either of the aërials it is necessary to know the magnitudes of the currents in them. To this end the platinum wire used on the ground side of the receiving aerial was replaced by the 4-volt, 1 candle-power, incandescent, and balanced in one arm of a Wheatstone bridge. Then alternating currents at 60 cycles were sent through the lamp while still in the bridge arm. This heated the lamp, lowering its resistance (being a carbon filament) and caused the galvanometer to deflect. The heating current was measured by sending it through an Olivetti hot wire voltmeter of known resistance.

Curve I. shows the relation between heating currents and deflections of the bridge galvanometer.

The lamp, still in the bridge arm, was now put back directly in the receiving aërial, and the galvanometer deflections observed as the self-induction in series with the aërial was varied, while there was a steady radiation of energy from the transmitter.

By reference to Fig. 3, the galvanometer deflections were translated into equivalent currents and Curve II. plotted. The natural period of the aërial would be proportional to the square roots of the localized self-induction, the capacity, also principally localized, being constant.

Hence, in Fig. 4, I have plotted current in aërial and square roots of self-induction.

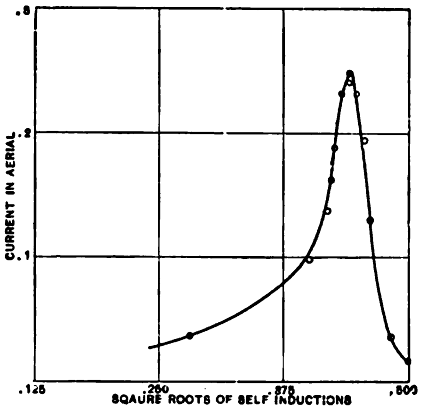

Fig. 4.

The self-induction was varied from 0.16 to 0.25 millihenrys. These self-inductions are certainly not correct for such high frequency, as they were obtained by calibration with a standard at low frequency. However, the difference is not large enough to affect the form of the resonance curve. For Curve II. the auto-transformer coupling of the transmitter was used, and the receiver consisted of four electric light cords, suspended from the ceiling, and all in series with a variable and previously calibrated self-inductance. The receiving aërial was 10 feet high and about 20 feet from the transmitter. The resonance point is fairly sharp and corresponds to a self-induction of 0.195 millihenrys. The capacity of the aërial was measured by charging it to 50 volts and discharging it into a standard condenser one hundred times in succession. The standard condenser showed no appreciable leak in 15 minutes and three determinations of the receiving aërial capacity agreed within 1 per cent. of $1.85 - 10^{-10}$ farads. This gives a period of 1.19×10^{-6}. If the self-induction were calculated or measured for high frequency this period would be slightly decreased.

Curve V. shows the increased sharpness of the resonance where the receiver as well as the transmitter is provided with an auto-coupling, and the little lamp placed as indicated in Fig. 5.

The receiver condenser circuit has the same period as the transmitter. Hence when the receiving aërial is out of tune with the transmitter, it is also out of tune with its own condenser circuit. and the resonance is very marked.

It will be noted that the currents are not nearly so large as in the aërial itself. The sharper resonance is attained at this expense, adapting this system, as Wien (*loc. cit.*) remarks, to short distances in territory in which are many other receivers, thus necessitating sharp tuning, and not requiring much energy.

Fig. 6 is obtained with a simple aërial for receiver, and the Tesla coupling for the transmitter. The resonance is not very sharp, but occurs for the same frequency as for Curves II. and V. Wien (*loc. cit.*) has shown that a magnetically coupled system radiates two trains of waves of different frequencies, and, in general, different damping coefficients. The lower resonance point at $\sqrt{L} = 0.575$ is for a period of 1.63×10^{-6} and doubtless corresponds to the second and less predominant wave-train. The damping is evidently much greater for this wave-length.

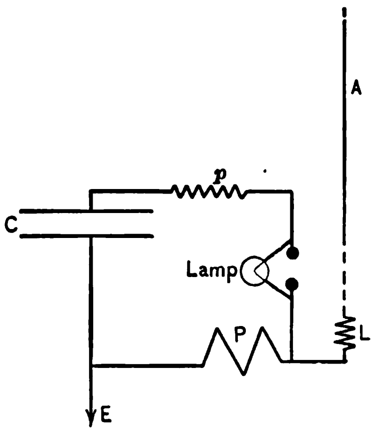

Fig. 5.

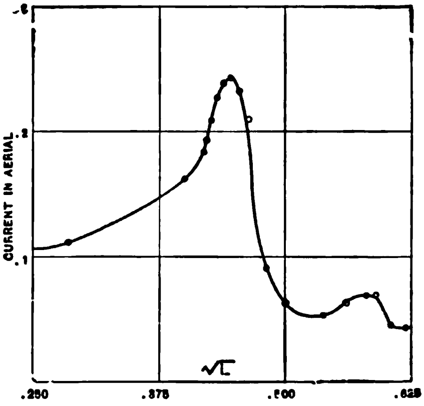

Fig. 6.

Fig. 7 shows the resonance effect when both sender and receiver are provided with the Tesla coupling, and the lamp is put across the spark-gap as in Fig. 3. The Tesla coil in the receiver acts as a step-down transformer, and hence the current is greater than in the aërial itself. The effective self-induction of the secondary of the Tesla coil of the receiver was 0.023 millihenrys, so that in order to get the range of self-inductance within the limits of the calibrated variable self-inductance, it was necessary to use an aërial of somewhat smaller capacity. This shifts the resonance point to $L = 0.237$, and also decreases the current in the receiver. If the same aërial had been used as for Curve III., the currents would have been even greater for Curve IV. It will be noted that the resonance, although much sharper than for a single aërial receiver, is not nearly as sharp as for the case represented by Curve V., while the energy received is very much greater. This also agrees with Wien's conclusion that the Tesla coupling is suitable for long distance work and where sharp tuning is not necessary. The curves are all steeper on the side towards greater self-induction, as is characteristic of electrical resonance curves in general.

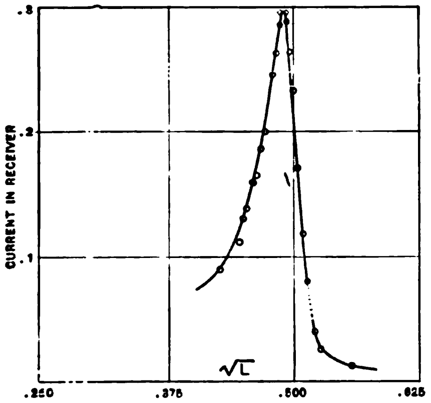

Fig .7.

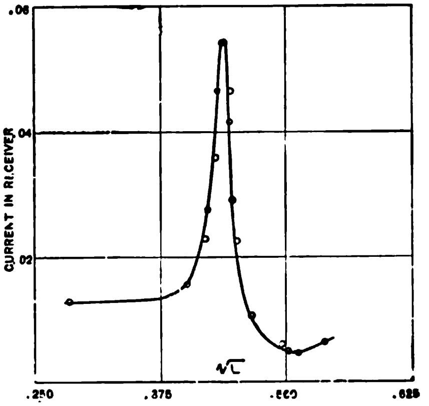

Fig. 8.

If the secondary of the Tesla coil is easily removable, it may be taken out and inserted in series with the aërial, and the latter joined to the primary by the auto-coupling. The aërial system will then still be very nearly in tune, a very slight decrease in self-inductance of the aërial being advisable, to allow for the mutual induction between primary and secondary, which is now absent. In this way one can pass from one coupling to the other without stopping to tune the transmitter each time. If the primary has no "ballasting" self-induction (as at p, Fig. 1) the transition is not quite so easy, since the lack of mutual induction now lengthens the primary period appreciably.

If the receiving circuit is far distant from the sender, one of them can be tuned to a small portable system consisting of a condenser with a variable inductance in series. The other system can then be also tuned to the portable system and both systems checked up occasionally to see if they are in tune.

PHYSICAL LABORATORY, UNIVERSITY OF WINCONSIN,
Madison, January 6, 1904.

ON THE CONDUCTIVITY PRODUCED IN RAREFIED GASES BY AN INCANDESCENT KATHODE.[1]

BY ERNEST MERRITT AND OSCAR M. STEWART.

THE increased electrical conductivity of rarefied gases produced by the employment of an incandescent kathode seems to have been noticed almost simultaneously by Hittorf[2] and by Edison. A result of this increased conducting power is strikingly shown in the case of the "Edison effect"[3] where the relatively small fall of potential in a glow lamp is sufficient to produce a current of several milliamperes through the gas separating the two ends of the filament, or between the filament and a third terminal which is positive with reference to it. The destruction of the filament can often be traced to this leakage current through the gas. Elster and Geitel have found that insulated conductors acquire a charge when placed near an incandescent solid in a partial vacuum, and have made an extended study of this effect. The explanation offered by J. J. Thomson[4] refers both of these phenomena to a common cause, namely the emission by the incandescent solid of negatively charged particles, which may either impart a static charge to a neighboring insulated body, or may act as the carriers of a current between the incandescent kathode and any suitable anode. Determinations of the ratio of charge to mass in the case of these particles indicate that they are similar to those which constitute ordinary kathode rays.[5]

There are many points of similarity between the behavior of an incandescent kathode and that of a kathode of suitable material, such as zinc, when illuminated by ultra-violet light. At sufficiently high vacua true kathode rays appear to be developed in both cases. In one case these are due to the action of heat; in the other case to the action of short light waves. The experiments here described were suggested by this similarity between the two classes of phenomena.

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[1] A preliminary account of the work here described was presented to the Physical Society, Feb. 22, 1902. (See Science, Vol. 15, p. 425.)

[2] Hittorf, Wied. Ann., 21, p. 119, 1884.

[3] Houston, Trans. Am. Inst. E. E., Oct., 1884, Vol. I.; Fleming, Phil. Mag., July, 1896; Preece, Proc. Roy. Soc , 38, p. 219; Elster & Geitel, Wied. Ann., 37, p. 315; Howell, Trans. Am. Inst. E. E., 14, p. 27, 1897.

[4] J. J. Thomson, Conduction of Electricity through Gases, Chap. VIII.

[5] J. J. Thomson, Phil. Mag., Vol. 48, p. 547, 1899.

In the case of the photo-electric discharge the current may be looked upon as consisting of two parts: (1) The current carried by the kathode rays produced by illumination; (2) the current carried by the ions that are developed by these rays in the surrounding air. That ionization is really produced by the slowly moving kathode rays of the photo-electric discharge has been shown by direct experiment.[1] We are not aware that there is any direct proof that the kathode rays from an incandescent solid possess the same ionizing power. But it seems highly probable that they do. If so, the current in the case of the Edison effect must also consist of two parts, one carried by the kathode rays themselves and the other by the ions produced by them. At high vacua we should therefore expect the phenomena to appear in their simplest form, since the conducting power of the slight remaining traces of gas would in all probability be inappreciable. For this reason our first experiments were made at high vacua, and experiments were afterwards made at pressures in the neighborhood of 1 mm., where the conducting power of the air proved to be an important factor. In the main the results obtained were such as would be anticipated from the above-mentioned analogy. But at high pressures a phenomenon was observed whose analogue in the case of the photo-electric discharge has not heretofore been detected.

Apparatus.

The apparatus was arranged as shown in Fig. 1, which shows the lamp at half its actual size. The filament[2] was of low resistance, and in our experiments took a current of from 1.2 amp. to 1.7 amp. with a p. d. between its terminals ranging from 6 volts to 8 volts. The filament was surrounded by the brass cylinder *CC* which served as anode. A galvanometer served to measure the current between *CC* and the filament. A battery *D* of adjustable e.m.f. in series with the galvanometer gave the desired potential difference between *F* and *CC*. The galvanometer current was in all cases so small that the resistance of the galvanometer and connections produced no appreciable fall of potential, so that the potential difference between *CC* and *F* was the same as the e.m.f. of the battery.

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[1] Merritt and Stewart, Physical Review, Vol. XI., p. 230, 1900.

[2] A number of filaments specially mounted for this purpose were kindly furnished by the Edison lamp works.

In most cases the circuit containing the galvanometer and the battery was connected to the negative terminal of the filament. The positive pole of the battery was connected to the cylinder *CC*, thus making it the anode. When the e.m.f. of the battery was zero, the cylinder was at the same potential as the negative terminal of the filament. In this case there would be no galvanometer current, since the discharge takes place only from that part of the filament that is at a *lower* potential than the other conductor. But when the e.m.f. had any value greater than zero the galvanometer was deflected.

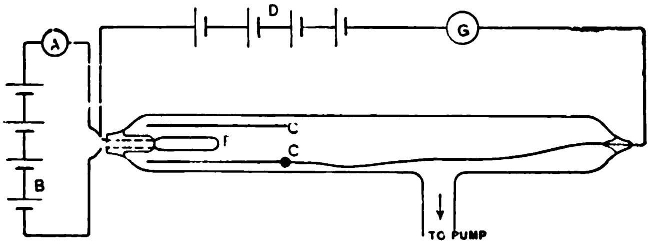

Fig. 1.

Upon reversing the battery *D* so as to make the filament the anode, the galvanometer showed no current unless the filament was heated to high incandescence; and even then the current was extremely small. This reversed current, already noticed by Fleming, has not been investigated in the work here described.

The magnitude of the current between *CC* and *F*, for a given e.m.f. and with all other conditions constant, was found to depend very greatly upon the degree of incandescence of the filament. This is well shown in Fig. 2. The upper curve is for an e.m.f. of 1.4 volts, or one Leclanche cell in the battery *D*, while the lower curve corresponds to an e.m.f. of 11 volts, or 8 cells. The vertical scale in the latter case is $\frac{1}{10}$ that of the former.

Since the galvanometer current was so greatly altered by changes in the lamp current, great care had to be taken to keep the latter constant. A storage battery was used as a source of e.m.f. But in determining the curves described below even the small fluctuations in the current from this battery were sufficient to introduce errors. An ammeter was therefore kept in the circuit and the current was adjusted, when this was necessary, before each reading.

A McLeod gauge was kept in connection with the pump throughout the work. Very little reliance can be placed on the indications of this gauge, so far as absolute values of pressure are concerned, owing to the small bore of its graduated tube. The gauge seemed to be especially sensitive to the sources of error to which all gauges of this type are susceptible. But the readings give an indication of the relative values of the pressure in different experiments. The gauge was also useful in indicating the degree of constancy of the pressure during the progress of a series of measurements.

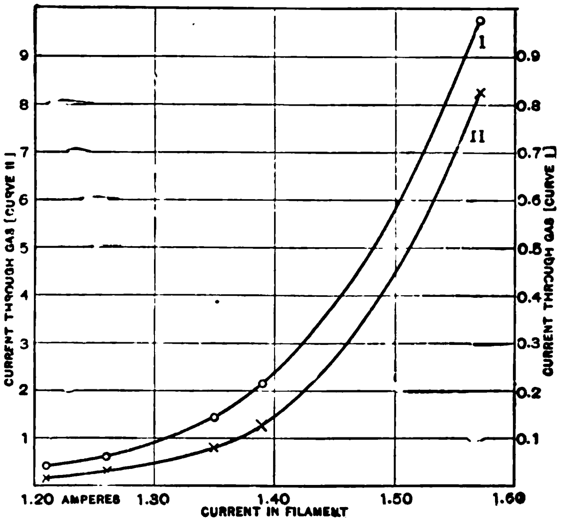

Fig. 2.

Experiments at High Vacua.

The character of the results obtained at high vacua is shown by the curves given in Fig. 3. In these curves the abscissas show the p. d. between filament and cylinder, while the ordinates give the corresponding values of the current. Each curve corresponds to a certain constant value of the current in the lamp, *i. e.*, to a constant temperature of the filament. During the determination of these curves the pressure as given by the gauge varied between .003 mm.

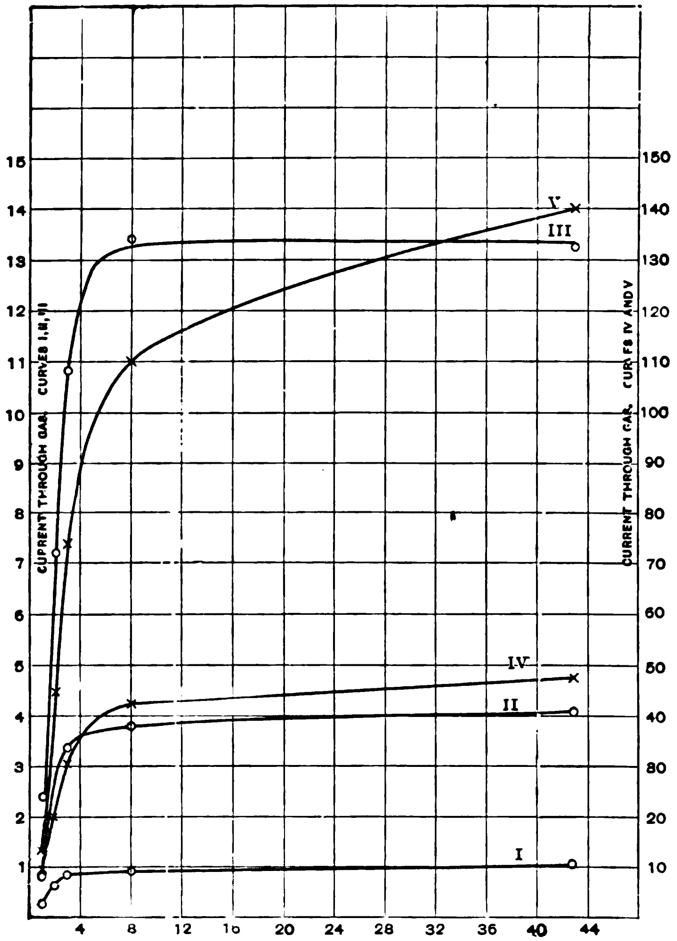

Fig. 3.

The unit in the case of the abscissas of these curves is the e. m. f. of one Leclanché cell — approximately 1.4 volts.

The curves were taken with the following values of the current in the filament.

Curve I. 1.2 amp.	Curve IV. 1.52 amp.
Curve II. 1.3 amp.	Curve V. 1.6 amp.
Curve III. 1.4 amp.	

Pressure, 0.003–0.007 mm.

and .007 mm. This variation was without appreciable influence on the results.

It will be noticed that the curves plotted in Fig. 3 show the characteristics that we should naturally expect in the case of gaseous conduction. The current at first increases approximately in proportion to the potential difference. A limit is soon reached, however, beyond which a further increase in the p. d. causes only a slight increase in the current; "saturation" has been reached. Saturation is more complete in the curves corresponding to low lamp currents, *i. e.*, to a relatively low temperature of the filament.

To some extent these curves are misleading. Under the conditions of the experiment very similar curves would be expected even if the galvanometer current did not depend at all upon the magnitude of the p. d. between filament and cylinder, but only upon its sign. It will be remembered that the galvanometer circuit was connected to the negative terminal of the filament, and that the current in the filament was sufficient to maintain a p. d. of from 5 to 8 volts between its terminals. At the beginning of each experiment, therefore, with no e. m. f. in the galvanometer circuit, all portions of the filament are positive with reference to the cylinder. Since it is only when the incandescent filament is a kathode that the Edison effect is observed, no current will flow. If a small e.m.f. is placed in the galvanometer circuit so as to make the cylinder positive, a portion of the filament near its negative end will now be at lower potential than the surrounding cylinder, and current can flow. As the potential of the cylinder is raised, a greater proportion of the filament becomes negative with reference to it, and can therefore take part in the transmission of current. When the potential of the cylinder is equal to, or greater than, the potential of the positive end of the filament, the whole incandescent surface has become kathode. If we assume that the current is in proportion to the kathode surface,

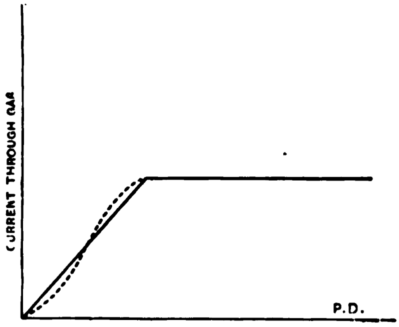

Fig. 4.

and that the fall of potential through the filament is uniform, we should expect the form of curve shown by the full line in Fig. 4, regardless of any direct dependence of current on p. d. Since the ends of the filament are cooled a little by conduction, the curve to be expected would be rounded somewhat as shown in the dotted line. This is exactly the form of curve obtained experimentally.

The important influence on the results of the difference of potential between different parts of the filament is well brought out in Fig. 5. The curves were taken under identical circumstances except that in one case the galvanometer circuit was connected to the negative terminal of the lamp filament, as usual, while in the other case it was connected to the positive terminal and the e.m.f. reversed. The character of both curves is readily explained then by the variation in the amount of the filament that was the kathode with respect to the cylinder.

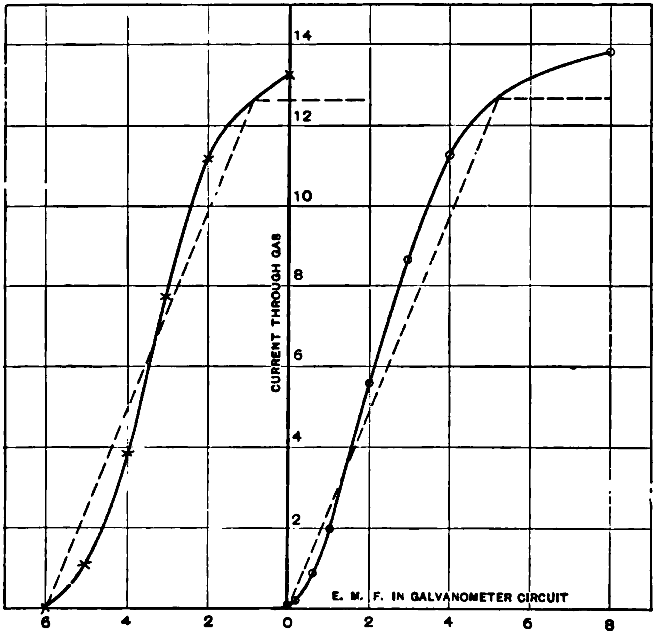

Fig. 5.

In Fig. 5 the curves to be expected from the known p.d. between the lamp terminals upon the assumption of a uniform drop through the filament are shown as dotted lines.

These curves, and others like them, show that the increase in current is a little more rapid, and continues longer, than could be accounted for by increase in kathode surface only. The current does depend somewhat upon the p.d. between filament and cylinder. But this dependence is slight. The number of negative ions developed at the incandescent surface is therefore increased very little by increasing the potential gradient. Lenard found that the behavior in the case of the photo-electric discharge at low pressures is similar to this, for the discharge current for a given illumination was changed very little by changes in e.m.f. It appears that the development of these negative ions, either in the case of an illuminated surface or an incandescent one, is more largely dependent upon some phenomena occurring at the surface itself than upon any electrical influences from outside.

It will be observed that there is nothing in the results obtained at high vacua to suggest that the phenomena are influenced by the small trace of gas left in the tube.

EXPERIMENTS AT LOW VACUA.

A series of curves taken under the same conditions as before except that the pressure in the tube was much higher had the same general form at low voltages as the curves shown in Fig. 3. In each case practically complete saturation was apparently reached at 10 or 11 volts. But when a larger potential was employed the current was found to be much larger than the saturation value. In Fig. 6 are shown three such curves. The vertical scale is different for each curve. The pressure in these cases was about 0.5 mm. Similar curves were obtained at a pressure of 0.16 mm., except that for a very low temperature of the filament (current in filament = 1.19 amperes) no abnormal increase in current was observed, even with an e.m.f. of 60 volts.

It was in these observations that what we have called the "creep" was first noticed. For low e.m.f.s the galvanometer promptly took a steady deflection; but when an e.m.f. greater than about 10 volts was employed the galvanometer current did not reach a steady value at once, but slowly increased for some minutes.

Curve I. in Fig. 7 shows the manner in which this change took place. The ordinates are proportional to the galvanometer deflections and the abscissas to time. In this case the current through the lamp filament was 1.50 amperes and the e.m.f. in the galvanometer circuit was 60 volts. As shown in the curve, readings were taken every ten seconds. Even at the end of 100 seconds the cur-

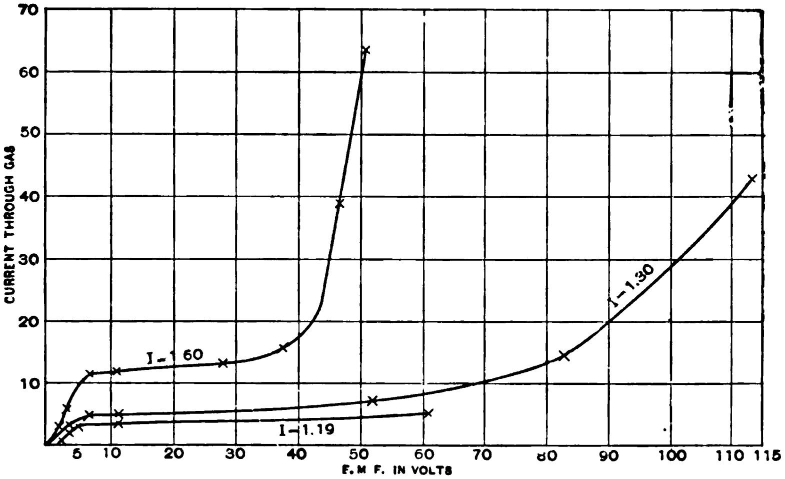

Fig. 6.

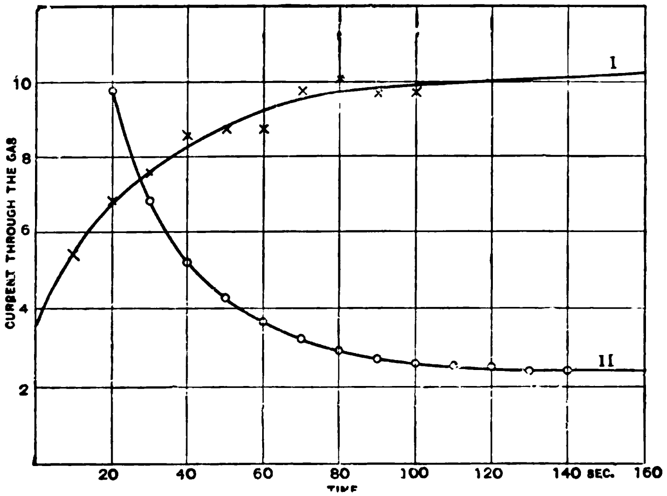

Fig. 7.

rent had not attained a steady value. Cases were noted where it required a much longer time than this for the current to reach its maximum value; in one instance an increase was observed for fifteen minutes after closing the galvanometer circuit. But for lamp currents greater than 1.74 amperes the galvanometer current, for all values of the difference of potential, reached its maximum apparently at once; certainly in a time too short to be observed with the galvanometer.

The data used in the curves of Fig. 6 were the values obtained after the deflections had become steady. The first deflection for a p. d. greater than 10 volts was in general approximately the same as that given by 10 volts; but the current increased slowly up to the value shown in the curves of Fig. 6.

If a rather high difference of potential between the filament and the cylinder was maintained for some time and then suddenly decreased, the reverse effect was obtained. For example, if the galvanometer circuit had been closed for some time with 60 volts, and if the e.m.f. was then suddenly decreased to 10 volts, the galvanometer current would at first be much larger than that corresponding to an e.m.f. of 10 volts as shown on the curve. It would, however, slowly decrease until it reached the value that would have been obtained had the higher e.m.f. not been used. Curve II. in Fig. 7 is a curve plotted from the observed values of the current at different times after the e.m.f. had been suddenly decreased from 60 volts to 11 volts. In this case the lamp current was 1.75 amp.— a value so great that the time *increase* could not be detected on applying the higher e.m.f.s. This slow decrease in the current was always noticed on suddenly changing to any lower p. d. from a p. d. greater than the one corresponding to the point of inflection of a curve like one of those in Fig. 6. Although the "creep down" was observed for the higher lamp currents, the duration of it was less than in the cases where the values of the lamp current were those corresponding to cases that gave the "creep up."

The rate of decrease of the galvanometer current on changing from a higher to a lower e.m.f. was to a large extent independent of other changes in the connections. For example the decrease for a given time after the higher e.m.f. was cut out was practically the same whether (1) the lower e.m.f. had been connected all the intervening time or (2) the circuit had remained open, up to this time, or (3) the cylinder had been connected directly to the filament.

DISCUSSION.

It is clear from the experiments here described that the phenomena are much simpler at high vacua. The incandescent filament still discharged negative electricity, even in the highest vacuum that our pump could give. It seems probable, therefore, that the electrons by which the charge was carried come from the incandescent body, rather than from gases in contact with it.

The resemblance between the behavior of an incandescent kathode and an illuminated kathode, already referred to at the beginning of this article, is too striking to be overlooked. In each case the phenomena are primarily due to the emission of negative electrons by the surface in question. In one case it is light — more especially ultra-violet light — that acts as the agent to bringing about the emission of such electrons. In the other case the high temperature of the surface produces the same result. The number of negative particles sent off in unit time depends in one case upon the intensity of the illumination; in the other case upon the temperature of the surface. In neither case is it largely influenced by the electric field, provided only that the direction of the field is such as to make the electrode a kathode.

At high vacua the kathode ray particles are the sole carriers of the current, and since their number depends chiefly on the degree of incandescence the curves show saturation at low values of the e.m.f. As the pressure is increased the air surrounding the kathode becomes an important factor. As the p. d. is increased the kathode rays will move at an increasing speed, and will finally move fast enough so that upon colliding with the molecules of gas these will be ionized. The ions thus formed will participate in the conduction between the filament and the cylinder, so that the current will again increase with the e.m.f. An explanation is thus offered of the form of the curves shown in Fig. 6. Similar curves have been observed for the photo-electric discharge by several observers.

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[1] Kreusler, Beibl., 22, p. 698; v. Schweidler, Wien. Sitzungsber., 107, p. 881 and 108, p. 273, 1898; also Beibl., 23, pp. 513 and 585.

Townsend has also observed a somewhat analogous phenomenon in the case of the conduction through gases that have been ionized by the action of Röntgen rays.[1] The effects observed by him were satisfactorily explained upon the assumption that the negative ions produced were able to ionize other portions of the gas, just as kathode rays do, provided that the conditions were such as to enable them to acquire a certain minimum speed between collisions. Curves similar to those shown in Fig. 6 were also obtained by McClelland[2] in the case of the current passing between a hot platinum kathode and a cold anode.

Although the hypothesis of ionization by collision at first appears to afford an entirely satisfactory explanation of the results obtained at low vacua, yet the various peculiarities of the "creep," and especially its long duration, offer serious objections to this explanation. Many attempts were made to throw further light on this phenomenon. If it were merely a case of a slow change in the ionization in the gas, the conductivity might be expected to last a short time after the circuit through the filament was broken. But the galvanometer current dropped at once to zero when the lamp circuit was broken. Yet if the lamp circuit was at once closed again it was found that the increased conductivity was still present. Suddenly reversing the direction of the e.m.f. in the galvanometer circuit also brought the needle promptly to a vibration about its zero.

An e.m.f. of 60 or 80 volts was applied long enough to obtain a steady current, and the galvanometer circuit was then broken for a definite time, from 10 to 30 seconds. On closing the circuit the galvanometer current was found to be somewhat less than its steady or maximum value, but still much greater than if the circuit had not previously been closed. The current would creep up to the value it had before the circuit was broken; but the fact that it was initially larger indicated that the increased conductivity of the tube had in part remained during the time the circuit was broken.

Reversing the e.m.f. in the galvanometer circuit for 20 seconds had no appreciably different effect from that of merely breaking the galvanometer circuit for the same time. The conductivity decreased apparently less if the lamp circuit alone was broken than if the galvanometer circuit alone was broken, *i. e.*, after keeping the lamp circuit open for 20 seconds the galvanometer current was larger than if only the galvanometer circuit had been broken for the same length of time. Breaking both circuits simultaneously for 30 seconds apparently produced even less diminution of the increased conductivity than breaking the lamp circuit alone.

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[1] Phil. Mag., Series 6, Vol. I, p. 198. 1901.

[2] Cambridge Philosophical Proceedings, Vol. 11, p. 296, 1902.

These observations show that the gas in the tube does not remain a conductor for any considerable length of time. Even if a current too small to deflect the galvanometer should flow, the gas would rapidly lose its ions and its conductivity. Yet, as shown, the increased conductivity is affected little, if any, by breaking the lamp circuit.

It therefore appears that the creep cannot be explained simply by the ionization of the residual gas. We are led to suggest that the effect is due rather to some gradual change in the incandescent surface, this change being of such a character as to increase the rate at which kathode rays are produced; when the filament is no longer negatively charged, or when it is allowed to become cold, the surface gradually returns to its original condition. In forming any opinion regarding the nature of this assumed change in the incandescent surface we must bear in mind the fact that it occurs only at low vacua; at high vacua nothing abnormal was observed. It is therefore clear that the presence of an appreciable amount of residual gas is essential. The temporary nature of the change in question shows that it cannot be due to oxidation of the carbon surface, or to any similar chemical action. But the results may be satisfactorily explained if we assume that something is deposited on the surface without uniting with it chemically. The material deposited must have a positive charge, for it is only when the filament is negative that the effect is observed.

When considered from this point of view the phenomena of the creep effect have many points of similarity with cases of excited radio-activity. One is tempted to believe that an active gas is liberated by the hot carbon and that the negatively charged filament acc
porary radio-activity in the same way that it would do if

by the emanations of radium or thorium. There is, however, one peculiarity in the effect which shows this explanation to be untenable. The change in the filament which caused the creep persisted for several minutes, even if the current in the filament was broken ; but no current could be detected in the galvanometer while the filament was cold. It seems, therefore, that the material deposited on the filament does not possess in itself any marked power of ionizing the gas; it merely intensifies the effect of incandescence. The phenomena are more satisfactorily explained if we assume that the deposit on the filament produces a condition analogous to polarization in a voltaic cell. If the positive ions attracted to the surface experience a certain difficulty in giving up their charges, a double layer will be formed at the surface, positive just outside and negative within. This will greatly strengthen the electric field at the surface, so that the tendency for negative electrons to escape from the carbon will be increased. It seems surprising that such a double layer is not at once destroyed when the e.m.f. is reversed. But the porous character of the carbon probably permits the positive ions to penetrate to a considerable depth, so that they cannot be quickly removed even by a reversed field. For the same reason the polarized condition requires an appreciable time for its complete development.

It is hardly to be expected that the negatively charged filament itself can be the source of the positive ions which cause this polarization ; these come rather from the residual gas. It is evident therefore that the effect can only occur at relatively high pressures. The formation of the assumed layer, and the consequent "creep" effect, can only take place when positive ions are present in the gas. But there is nothing to produce ionization except the kathode rays from the hot carbon ; hence we cannot expect the polarized layer to form until the velocity of the kathode rays is sufficient to produce ionization in the surrounding gas. In other words the creep effect will only be observed when the e.m.f. in the galvanometer circuit exceeds a certain critical value. For e.m.f.'s less than this we have the ordinary phenomena of conduction in a gas with ionization at the negative terminal only ; the gas itself has no influence upon the conduction, except so far as it alters the speed of the negative ions. No positive ions are present. For higher electromotive forces the phenomena are modified in two ways: (1) The kathode rays produce ionization in the air, which now participates in the conduction; (2) positive ions now being present, some of these collect on the carbon filament and form there a positively charged layer. This increases the ease with which negative electrons escape from the hot carbon, so that kathode rays are produced in greater intensity. When the critical value of the electromotive force is exceeded there are therefore two reasons for an increase in current, and the sudden bend in the curves of Fig. 6 is a natural result.

Since the MS. of the preceding article was sent to the printer, a preliminary paper has been published by J. Stark, which deals in part with experiments upon the same subject.[1] The arrangement of apparatus in these experiments was somewhat different from that adopted by us; and to this fact is doubtless to be ascribed a part of the difference in the results obtained. But we are unable to account for all of the differences in this way.

The filament employed in Dr. Stark's experiments required a potential difference of 6 volts at its terminals to bring it to the proper incandescence. This is approximately the same p. d. that was used in our own work. Instead of a cylindrical anode, however, a wire was used, this being placed in a side tube at a distance of 6 mm. from the filament. At pressures ranging from 0.029 mm. to 4.2 mm. the curves connecting the e.m.f. and the current through the gas show a general resemblance to those plotted in Fig. 6 on p. 247, but differ from them in three ways, viz.: (1) the rapid increase in conductivity, which indicates the beginning of ionization by collision, begins at about 11 volts, instead of at about 30 volts; (2) a second more rapid rise in the conductivity of the gas occurs at about 27 volts; (3) at about 40 volts the current reaches a new saturation value, far greater however, than the value corresponding to e.m.f.s below 10 volts.

The sudden increase in conductivity observed by us seems to correspond to the *second* break in the curve obtained by Stark. That this point corresponds to the beginning of ionization by collision in the nitrogen remaining in the tube, as suggested by Stark, seems to us quite probable. In fact this is practically the explanation reached by us. The third stage mentioned by Dr. Stark, corresponding to potentials higher than 40 volts, was not observed in our experiments; there was nothing to suggest renewed saturation, even at potentials as high as 115 volts. This may perhaps be due to differences in the form and dimensions of the apparatus. We are at a loss, however, to account for the absence in our curves of the first stage mentioned by Dr. Stark. No sudden increase in conducting power in the neighborhood of 11 volts was observed in our experiments. Dr. Stark explains the break in his curves at about 11 volts as due to the ionization of mercury vapor, and therefore sets the ionizing potential for mercury vapor at 11 volts. Since the tube used in our experiments remained in connection with the pump for days at a time there is every reason to believe that mercury vapor was present. Yet there is no indication that it participated in the conduction in any way. This is true not only in the case of the observations at the relatively high pressure of 0.5 mm. (Fig. 6) but also in the case of the observations at low pressures (.003 mm.) shown in Fig. 3. The latter observations seem especially well adapted to show the influence of the mercury vapor if such influence exists, for the disturbing effect of other gases is reduced to a minimum. Unfortunately the observations of Dr. Stark do not extend to pressures below 0.029 so that no direct comparison of our results is possible.

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[1] Physikalische Zeitschrift, Vol. 5, p. 51, Jan. 15, 1904.

In this connection the great difficulty that is always experienced in completely freeing a carbon filament from occluded gases should not be forgotten. In order to accomplish this so far as possible we were in the habit of running the filament during the process of exhaustion at a higher temperature than that used when making measurements. Such a procedure was indeed absolutely necessary in the work at low pressures, since the liberation of gas by the filament made it otherwise impossible to maintain a high vacuum. When it is remembered that some liberation of gas will still occur even when this precaution is taken, and that it will occur with greater rapidity when the temperature of the filament is high, certain peculiarities in the curves shown in Fig. 3 become significant. Curves I., II. and

III. in this figure show practically complete saturation, with no indication of ionization by collision. There are the curves corresponding to small lamp currents and therefore low temperatures. In Curves IV. and V., for which the temperature of the filament was higher, the saturation is not so complete. May it not be that we have to deal here with ionization of the gas liberated from the filament? And may it not be that the effects ascribed by Dr. Stark to mercury vapor were in reality due to some readily ionized gas given off by the filament?

Dr. Stark does not appear to have observed the phenomenon referred to by us as the "creep." It seems probable that the filament was kept at so high a temperature in his experiments that steady deflections were reached almost instantly.

FIBERS RESEMBLING FUSED QUARTZ IN THEIR ELASTIC PROPERTIES.

By K. E. Guthe.

THE advantages of quartz fibers as suspensions, principally their small elastic fatigue, great strength and the possibility of drawing very fine threads, have led to their use in a great many important investigations where fine suspensions and a steady zero-point are required.

In my work suspensions were needed able to carry a load of 500 g. and more, and at the same time having as small an elastic fatigue as possible. Naturally fused quartz was selected as the substance promising the best results. Such fibers must be rather thick, from 0.1 to 0.2 mm. in diameter. Since it was desired to draw them at least one meter in length, it required the melting of a rather large bead free of air bubbles. The process of building up quartz rods is known to be rather tedious. Shenstone's method[1] is simpler and consists of heating the crystals to about 1000° C. and suddenly quenching them in cold water. The crystals after such treatment are not shattered and do not break when brought into the oxy-hydrogen flame. A stick of the proper dimensions is easily formed, containing however a large number of air bubbles. To remove these is a very tedious task and particularly exasperating, because quartz at the high temperature of the blowpipe flame is quite volatile, about one half of the mass evaporating during the process.

Whichever method is employed it means a considerable loss of time, if a great many fibers of the dimensions necessary for my work have to be drawn.

Boys[2] in his first paper on this subject mentions his experiments on a great many minerals, of which only a few, however, could be drawn into fibers, and these, he says, were far inferior to those made from fused quartz. I have also tried a great number of substances, all silicates of magnesium: Enstatite, olivine, serpentine and meerschaum, but without success. Only the amphibol-asbestos, $Mg_3Ca Si_4O_{12}$, in the ordinary mineral form as well as when specially prepared for chemical purposes, and the steatite or soapstone, $Mg_3H_2 Si_4O_{12}$, give clear beads before the oxy-hydrogen blowpipe. These under proper precautions can be drawn easily to fibers of the desired dimensions. The soapstone is especially easily worked and gives fibers of practically the same elastic properties as those of quartz. Since the method of making them is so simple and requires little time, a short description may be of general interest.

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[1] Shenstone, Nature, Vol. 64, p. 65, 1901.

[2] Boys, Phil. Mag., Vol. 23, p. 489, 1887.

The soapstone, when heated to a high temperature, becomes exceedingly hard, and is used commercially under the name of "lava" for making apparatus intended to be able to stand high temperatures, for example, tips of gas burners. While it cannot be melted before an ordinary blowpipe, it does so before an illuminating gas-oxygen jet and forms a clear bead, usually of a greenish tint due to the presence of a trace of iron. The original soapstone or the "lava" will do equally well, the most convenient form being small cylindrical sticks.[1] If the flame of the blowpipe is too long or the mixture of the gases not well adjusted, the substance will boil violently, while with a small, quiet flame it melts without boiling, a slight development of gases being noticeable only at the upper, cooler part of the bead. After taking the pearl out of the flame, the thread is drawn, its thickness depending upon the temperature and rapidity with which it is drawn. Very fine fibers can thus be secured. The fibers should not be heated after being drawn. In a Bunsen burner, for instance, they will immediately become white and break to pieces.

Elastic Fatigue. — It is very well known that fine quartz fibers show hardly any elastic fatigue,[2] but with thicker fibers of 0.1 to 0.2 mm. diameter, the effect of elastic fatigue became quite apparent. Careful experiments showed that small twists, or twists of small amplitude do not affect the zero-point, while larger twists being continued for several minutes would displace the zero-point. The apparatus used allowed a turning of the torsion head while the lower end of the fiber was held in its original position. After release the zero could be redetermined in a few seconds and the slow disappearance of the effect of elastic fatigue observed. With fibers 70 cm. long and 0.1 mm. diameter, the displacement after release from a torsion of 360° lasting 5 minutes, amounted to as much as 2 in 3,000. Fibers made of steatite showed about the same effect, which is however very much smaller than any other substance experimented with, and about one half to one third of that shown by steel or phosphor bronze.

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[1] Such cylinders 3 mm. in diameter and 7 cm. long, giving colorless transparent beads about 5 mm. in diameter, were obtained from the Chattanooga Sunlight Lava Manufacturing Company.

[2] Boys, l. c., p. 496; Threlfall, Phil. Mag., Vol. 30, p. 113, 1890.

For these experiments the quartz and steatite fibers had been silvered at their ends, then coppered and finally soldered into large brass pins clamped securely in the supports. Thus the elastic fatigue observed cannot be attributed to an effect of the material with which fibers were fastened to the other parts of the instruments.

Tensile Strength. — The tensile strength of very thin quartz fibers is quite large: 10×10^9 dynes per cm.^{2}, but it decreases appreciably with increasing thickness.[1]

The following experiments show the same result. From Table I. it is seen that the tensile strength of the steatite fibers is at least as large as that of quartz. For comparison the values given by Boys, (B), are added. The decrease of tensile strength for the

TABLE I.

Quartz.		Lava.	
Diameter.	Tensile Strength.	Diameter.	Tensile Strength.
(B) 0.00048 cm.	11.5×10^9 dynes / cm.^{2}		
(B) 0.00175	8.0		
0.0075	6.21	0.006 cm.	13×10^9 dynes / cm.^{2}
0.0095	6.91	0.0095	9.96
0.010	6.16	0.010	9.11
0.015	4.5	0.011	7.19
0.0175	3.91	0.0135	6.92
0.018	4.08		

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[1] Boys, Phil. Mag., Vol. 30, p. 116, 1890.

thicker fibers is very striking. For the thickest fibers it is, however, still as large as that of brass.

Coefficient of Simple Rigidity. — The torsional coefficient was determined by the well-known method of vibration. The diameter and length of the fibers were carefully measured, a cylinder made of Tobin bronze was suspended by the fibers and the period of the torsional vibrations determined by means of a chronometer. Then

$$n = \frac{8\pi IL}{r^4 T^2}.$$

Since it became apparent that different fibers of the same substance gave slightly different values, and since the diameters of the fibers were measured only with an accurate micrometer, no correction for the coefficient of expansion was made.[1] The mean of a number of experiments gave for quartz $n = 3.4 \times 10^{11}$; for the steatite fiber a value from 2.6 to 4.2×10^{11}. Also in this respect the new fiber almost exactly equals fused quartz. The temperature coefficient of the torsional constant of quartz is given by Threlfall as $+0.000133$; by Barnett[2] as $+0.000115$; I obtained $+0.000149$. Steatite does not show the remarkable property of becoming more rigid at higher temperatures. Its temperature coefficient is negative, $a = -0.000193$. The results obtained are given in Table II. and plotted in Fig. 1.

TABLE II.

Quartz.			Lava.		
Temp.	Period.	n	Temp.	Period.	n
8°.5	8.3083	3.4044×10^{11}	11°.45	8.7507	3.9830×10^{11}
19°.0	8.3020	3.4096	17°.10	8.7556	3.9777
22°.45	8.2997	3.4115	22°.05	8.7590	3.9755
26°.2	8.2973	3.4134	26°.75	8.7625	3.9723

Coefficient of Expansion of Fused Steatite. — The following experiments were made by Mr. L. G. Hoxton, of the Bureau of Standards, using a rather thick fiber of fused steatite.

The length between two fairly well defined marks 110.4 mm.

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[1] See also Threlfall, l. c., p. 108.

[2] Barnett, PHYS. REV., Vol. 6, p. 119, 1898.

apart was compared at different temperatures with that of the standard nickel steel decimeter No. 43, belonging to the Bureau and furnished with a certificate from the Bureau International des Poids et Mesures, which gives its linear coefficient as $\alpha = 0.96 \times 10^{-6}$. In the following table the differences between the length of the fiber and the standard are marked F—NS. In the third column is given the linear coefficient of expansion counting from the lowest temperature and in the last the number of observations made for each temperature.

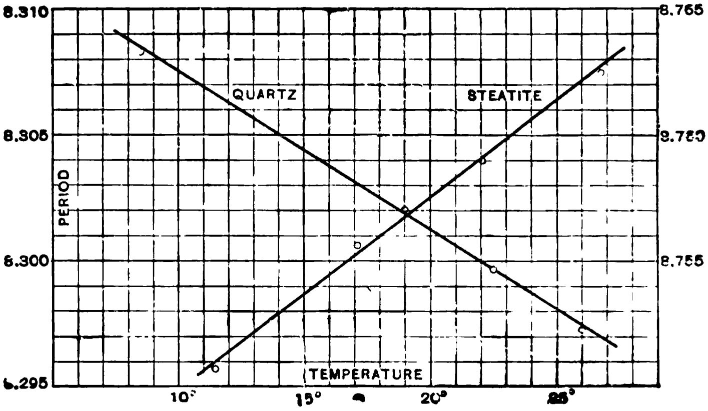

Fig. 1.

TABLE III.

Temp.	F—NS.	α	No.
+ 19°.31	+ 10.3 μ	0.0_5317	5
+ 3°.56	6.4	0.0_558	7
− 2°.08	2.8		5
+ 21°.8	12.4	0.0_5365	4

The average relative coefficient is found from the normal equation

$$1059.4\, x = 410.1 \frac{1}{110400}$$

$$\therefore \quad x = 0.00000350.$$

The absolute linear coefficient of expansion is therefore

$$\alpha = 0.0000045.$$

The comparisons were made on a Zeiss horizontal comparator, which allows a direct reading of 1.0 μ.

An attempt to obtain a fiber with a zero temperature coefficient by melting quartz and steatite together was unsuccessful. As soon as too much quartz is present, the bead loses its transparency. If beads made of soapstone should not be clear, it is generally due to an excess of quartz in the substance. In such a case the addition of a small amount of magnesia or magnesium carbonate will clear up the bead.

Index of Refraction of Fused Steatite. — Two small prisms were ground from steatite beads and their index of refraction for sodium light determined by the method of minimum deviation. The instrument used was a spectrometer reading to half minutes. Table IV. contains the results.

TABLE IV.

	Angle of Prisms.	Min. Deviation.	μ
Prism 1	60°3′	44°1′	1.576
Prism 2	60°4′	44°17′	1.578

Also for these determinations I am indebted to Mr. L. G. Hoxton.

From the above comparison we conclude that we have found in fused steatite a substance which shows all the characteristic properties of fused quartz. The method of drawing fibers from it is very simple, and since the substance is easily secured (an old jet of a gas burner will furnish a large number of fibers) these fibers may with advantage be used, where economy of time is an important question. One more advantage lies in the easy handling of the fiber. While thick quartz threads break easily when bent, those of steatite may be bent considerably more without breaking.

Barnett[1] working with fibers from 0.005 cm. to 0.007 cm. in diameter did not detect any time effect upon the period. But a distinct effect was found by me with either quartz or steatite fiber. The quartz fibers became more rigid in course of time, a behavior resembling that of metals.[2] Professor Carhart and the writer have found, however, a decrease of rigidity in the case of phosphor bronze.[3] Continued vibrations, especially of very large amplitude, seem to have a distinct influence upon this "settling down" to a steady state, if such can be obtained. Investigations are carried on concerning this time change, in order to determine whether different specimens of quartz will differ in their behavior — ours contained quite a large amount of strontium — or whether the difficulties are to be attributed simply to the size of the fibers.

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[1] Barnett, l. c., p. 116.

[2] Nichols and Franklin, El. of Phys., I., p. 99.

[3] Carhart and Guthe, PHYS. REV., Vol. 9, p. 292, 1899.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

THE CONTINUOUS METHOD OF STEAM CALORIMETRY.

By Joseph H. Hart.

THE continuous method of steam calorimetry was devised as the result of an attempt to measure the variation of the specific heat of a body in a magnetic field. Nearly all the known calorimetric methods were used and the difficulty of getting concordant results in consecutive experiments beyond the third significant figure without special refinement in the method and in the observations was early recognized. The present method while inapplicable to that problem was thereupon developed as capable of a much greater accuracy with less refinement in the method than any method hitherto employed.

If a stream of water at a temperature θ_1 is passed through a worm which is immersed in a steam bath and emerges at a temperature θ_2 the heat absorbed by the water is $mS(\theta_2 - \theta_1)$ where m is the mass of water passed through and S the mean specific heat between θ_2 and θ_1. If all the heat absorbed is obtained by direct condensation of steam alone, we have the equation,

$$ML = mS(\theta_2 - \theta_1),$$

where M is the mass of the condensed water and L the latent heat of steam.

In the practical development of the method the process was made continuous. The condensed water was collected and drawn off continuously. This mass and the mass of the water which had passed through the worm were measured some time after an experiment so that complete attention could not be given to the determination of the temperature differences. Thus L or S could be readily determined, if the other was taken as known. Barnes' values of the specific heat of water were taken and a large number of experiments were made to determine L in order to test the efficiency of the method.

Many difficulties were encountered in the preliminary tests on account of the radiation and conduction from the walls of the calorimeter into the worm and many of the small details of construction in the worm and calorimeter are the result of much study. The measurement of the condensed water also presented difficulties which, it is believed, have been overcome. The construction given below eliminates the radiation and conduction of heat into the worm from the calorimeter, or at least satisfactorily accounts for it in the quantity of condensed water collected, both by theory and practice.

The prime requirement in the development of this method was the uniform production of a large amount of dry steam at constant pressure. The only way by which the temperature θ_2 could be kept constant, when the steam supply varied, was by regulating the velocity of the flow of the water (m) through the worm. This was found undesirable and a number of experiments were made to construct a satisfactory boiler. A slight change in the water level in the boiler was found to produce considerable change in the steam supply. This became at once evident by a change in the temperature θ_2, if all the steam supply was being condensed. Boiling by bumping also produced changes and external drafts on the boiler had an appreciable effect. The slightest complication in the construction of the boiler also produced considerable variations in the pressure. The boiler used in the final experiments gave very satisfactory results and is shown in Fig. 1. It is completely covered with an asbestos jacket, and is connected through a small intermediate compartment with an adjustable constant level apparatus. In the top is a water manometer with constant zero resulting from condensation of steam. Its dimensions are 40 cm. by 15 cm. by 25 cm. high. It was connected to the calorimeter almost immediately through a tube 10 cm. in diameter. This boiler was used for stretches of over fourteen hours without any attention whatever and with no appreciable change in the steam supply or in the pressure. The water manometer was very sensitive and showed small variations in the pressure when the calorimeter was connected to the boiler. When the condensation commenced, however, this variation diminished and the pressure could be made approximately constant throughout an experiment, after the rate of condensation had become constant, by varying either the heat supply or the size of the outflow tube from the calorimeter to the condenser. This steam pressure, constant throughout an experiment, was less than 0.5 mm. water pressure and was sometimes added to the barometric reading, but was more often totally neglected.

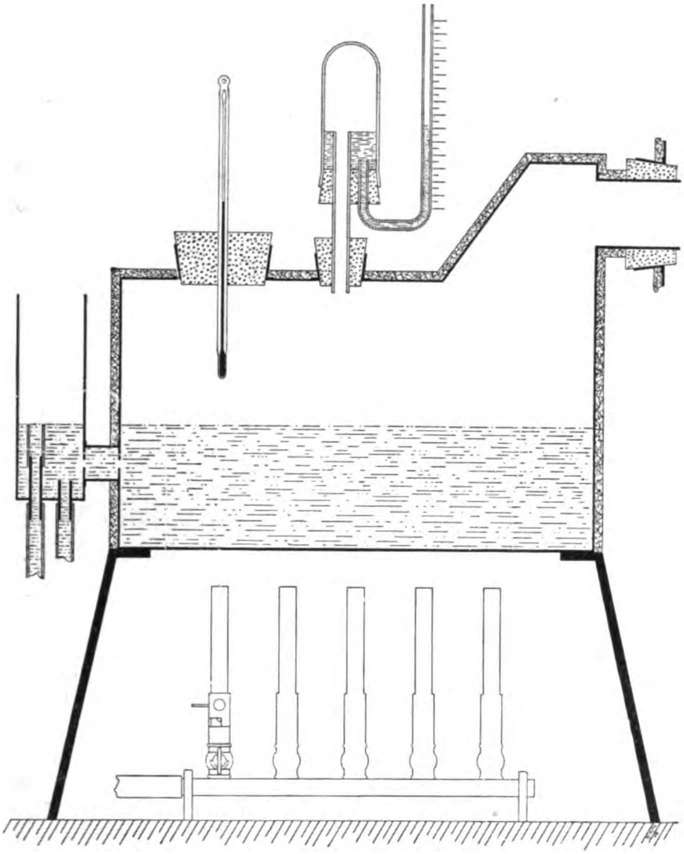

Fig. 1.

The calorimeter was a metal box 20 cm. by 20 cm. by 75 cm. high with a conical top and had an inlet and an outlet through large corks for the water (*m*), an inlet and an outlet for the steam and an outlet for the water condensed on the worm. The calorimeter was covered with a heavy asbestos jacket which prevented much condensation on the walls of the calorimeter. A cross section of the calorimeter and worm is given in Fig. 2. The worm was made of the thinnest sheet copper compatible with the necessary strength and consisted of a cylinder 3 cm. in diameter and 60 cm. long with a partition across it one quarter of the way from the upper end. This cylinder was then wrapped spirally with a thin strip of copper and another tight-fitting cylinder of very thin copper sheet was screwed on this, thus forming a worm, like a very long thin ribbon.

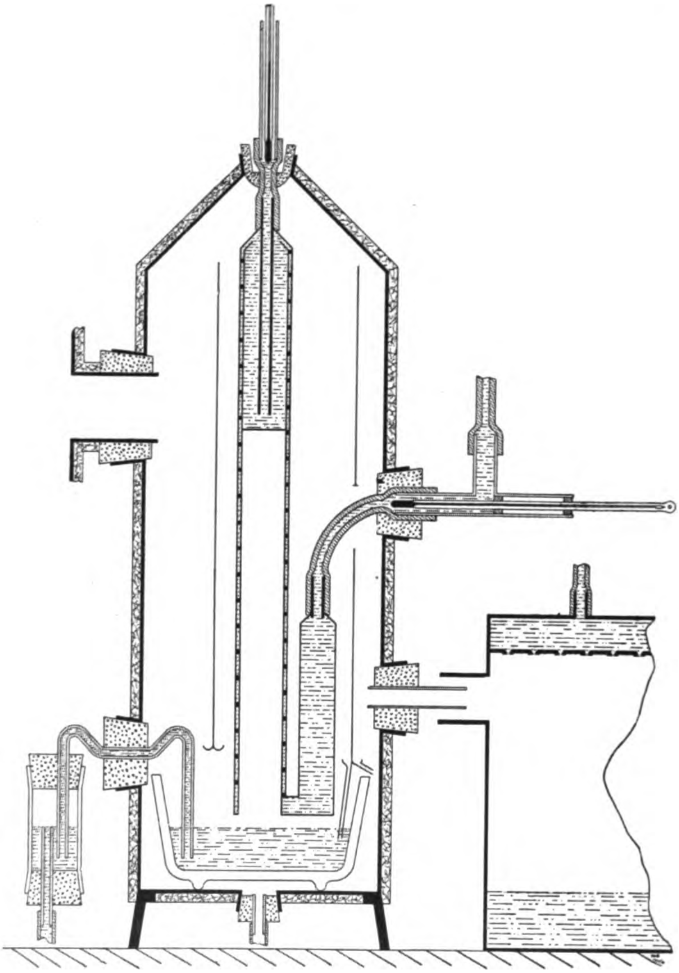

Fig. 2.

This worm was connected at the lower end with a reservoir of thin sheet copper 3 cm. in diameter and 15 cm. in height. The partition across the inner cylinder formed the base of the incoming cold water reservoir, which had for its sides and top the ribbon-like worm filled with warm water. The incoming water was carried by a tube to the bottom of this reservoir.

The object of this construction of the worm was to present a large heating surface for the steam, to have a large quantity of water heating constantly, and to keep the incoming cold water from close thermal contact with the steam, thus preventing a rapid local condensation of the steam. While a rapid local condensation of steam is undesirable, since the rapid cooling would tend to lower the temperature of the condensed water below the temperature of condensation, it is not necessarily detrimental to the method. For the condensed water, whatever its temperature may be soon after condensation, if it remains a sufficient time in the calorimeter, will in turn condense sufficient steam to raise it to the temperature of condensation.

The cold water was sent into the worm through a heavy rubber tube which was sealed, steam-tight, into a large cork at the apex of the conical top of the calorimeter. An air chamber surrounded a portion of the tube in the interior of the cork. The walls of the cork were cut at an angle so that the water which was condensed from the steam as a result of conduction through the cork to the cold water was collected with the water condensed on the worm. A cross section of this entrance together with the position of the thermometer is given in Fig. 2. The rubber tube was fitted over a glass tube which held the thermometer and through which the thermometer was read. The thermometer was completely immersed in the flowing water and did not touch the walls of the tube except at the top. The small exposed portion of the tube was wrapped with a two-inch layer of cotton. In this was a small curtain which was raised whenever the temperature was observed. Throughout the experiments, except when there was a very slow flow of water through the worm, the temperature of this thermometer was not 0.1° C. higher than a thermometer immersed in the supply tank.

The condensed water was collected in a heavy glass jar and siphoned off to a small reservoir outside in which the water stood at the same level. From this reservoir an overflow connected with large bottles in which the condensed water was stored during an experiment. These bottles were corked immediately at the end of an experiment and kept until measured. The water capacity of this system was found to be quite large and hence its sensitiveness to change in water level was small. From 3 to 5 grams of water could be added in the interior of the calorimeter without producing motion in the system. The sensitiveness of the system was much improved by diminishing the air pressure in the outer reservoir. This was done by an aspirator through a tube, not shown in Fig. 2, connected to the outer reservoir. The relief in pressure was made only at the beginning and end of an experiment. A number of experiments were made by passing known quantities of water into the inner receptacle and measuring the outflow. The aspirator was used for a very short time before water was poured into the vessel and again just as the flow was stopping. The difference in amounts of water put in and drawn off were less than 0.5 grams. This device concedes an error in an actual experiment on account of the extra condensation of from 20 to 30 c.c. of steam drawn over by the aspirator. This error, however, is small in comparison to the error resulting from the water capacity of the system.

The supply tank was about four times the size of the calorimeter and is shown in Fig. 3. It has a constant level attachment and was used to give a constant pressure and hence constant flow to the water passing through the worm. It was surrounded by a constant temperature bath and was made in this special form to give a constant flow of water at 0° C. The incoming water was cooled by ice or a mixture of ice and salt and water at 4° C., collected at the bottom. On being further cooled it rose in the other side of the tank and was drawn off at 0° C. approximately through the worm. The supply tank, however, has not as yet been used in this capacity. Experiments have been made in which the temperature of the water flowing into the worm has had various constant values ranging between 10° C. and 27° C.

The water flowing from the worm was drawn off through a thick heavy rubber tube, curved so that the water condensed on its surface would flow back into the condensed water reservoir. The tube was sealed into the cork steam tight and was forced over a T-tube in the interior of the cork as shown in Fig. 2. A thermometer was immersed in the water in the tube as shown in the diagram and was kept from touching the sides of the tube by rubber bands at the other end of the tube. The entire T-tube was wrapped with a two-inch layer of cotton and a small curtain removed when the temperature was observed. A small shelf was placed in the cork

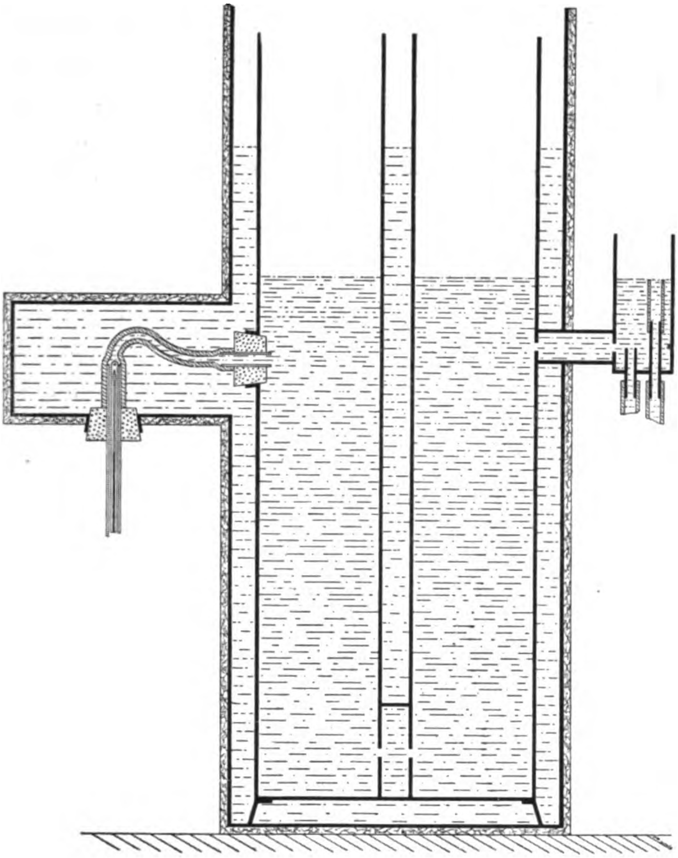

Fig. 3.

in the interior of the calorimeter above this outlet in order to prevent water which was condensed on the sides of the calorimeter from flowing in the condensed water reservoir. While a certain error exists at this outlet to the worm due to conduction of heat through the cork to the water, it is very small on account of the high temperature of the water. It is probably more than counterbalanced, however, by a transfer of heat from the water externally.

Also a certain quantity of heat was lost by conduction externally through the siphon forming the condensed water outlet. This cooling of the siphon and the condensed water contained in it caused an extra condensation of steam on that portion of the siphon inside the calorimeter. The upward bend in the siphon at this point is intended to prevent such condensed water from flowing back into the condensed water reservoir.

The condenser was of a special type as shown in Fig. 2. It was constructed after all other types of condensers used in the laboratory had proved inefficient. In construction it is simply a metal box with a shower of water inside and a pool of water at the bottom with an overflow. The falling water acted as an aspirator and a slow steady stream of air was drawn in through the steam inlet. This prevented any escape of steam into the room. The condenser was capable of condensing all the steam produced by the boiler.

It was thought that the radiation loss as a whole into or from the worm would be large, but this was found to be not so. In the Joly steam calorimeter the radiation loss amounted to 4 or 5 mgm. of condensed water per hour. The radiating surface was small in this calorimeter, but the temperature gradient outward was approximately the same over the entire inner surface of the calorimeter.

In the continuous steam calorimeter, however, the temperature gradient was very steep throughout a large portion of the worm so that in many of the experiments the radiation was internal. The heat was radiated from the walls of the calorimeter into the worm and raised the temperature of the water passing through it about 0.1° C. The radiation correction, however, depended on the values of the temperature of the water flowing in and out of the worm. If this water went into the worm about the temperature of the room and emerged at nearly the temperature of the steam, heat was radiated both to and from the worm and the radiation loss became negligible for some experiments, within the limits of accuracy used in the experiments. However, to measure and correct for radiation, a very thin sheet copper cylinder was used. It almost completely covered the worm, as shown in Fig. 2. It was freely exposed to the action of the steam and rapidly acquired its temperature. A small gutter was constructed around the base of the internal surface of this cylinder and connected with the condensed water reservoir. A similar gutter around the base of the external surface of the cylinder connected with the walls of the calorimeter. The temperature of this copper cylinder was maintained at approximately the temperature of the steam and radiation occurred in both directions, to the walls of the calorimeter and to the worm. The loss of heat from the cylinder to the worm was replenished by condensation on the cylinder and this water was collected in the condensed water reservoir. The condensed water which collected on the cylinder on account of radiation to the walls of the calorimeter was drawn off with the water condensed on the calorimeter walls. There is no radiation under these conditions from the worm outward, not even if the worm acquired the temperature of the steam.

The average temperature of the water going into the worm and that of the water coming out of the worm was obtained in a number of different ways. The thermometers were used to 0.1° C. and were calibrated and standardized before use in ice and steam. No stem corrections were made and errors due to the rising and falling of the mercury column were totally neglected since such a large number of readings were taken under such a variety of conditions. The temperature of the inflowing water never varied as much as 1° C. throughout the total time of the experiment. This change was generally very slow and uniform and readings taken at regular intervals gave a fair average temperature. The variation in the specific heat of water with temperature was totally neglected in considering this average temperature. The temperature of the water flowing from the worm was oscillating within narrow limits. The size and shape of the reservoirs in the worm were varied to produce more uniform mixing of the water before egress. A slow oscillation of about 2° C. in amplitude was generally present in the hot water thermometer. This oscillation of temperature could be followed absolutely if the thermometer was read at ten or twenty second intervals. A series of experiments on temperature averages carried on conjointly by this method and by an average of readings taken uniformly at three minute intervals, differed only in the fourth place. The temperatures θ_1 and θ_2 were therefore obtained from a series of readings at one, two, or three minute intervals, depending on the quantity of water which was passed through the worm.

The details of operation of a specific experiment were as follows: The boiler was started and the rate of flow through the worm for a definite temperature determined and then made permanent. The apparatus was kept in operation for several hours before beginning an experiment in order to make temperature conditions constant. When ready to begin an experiment, the aspirator was turned on momentarily and the water in the condensed water reservoir reduced to a certain definite level. Immediately the outflow tubes for both m and M were introduced simultaneously into large collecting bottles which possessed only small capillary openings for the escape of air when the bottle was being filled. The temperatures θ_1 and θ_2 were read alternately at regular intervals. Generally from 100 to 250 readings of each temperature were obtained.

At the end of an experiment, the aspirator was again turned on and the water in the internal reservoir reduced to the same level as at the beginning of the experiment. The tubes were removed simultaneously and the bottles immediately sealed. The barometer was read immediately before and after an experiment. The collected water was allowed to cool to the same temperature, generally that of the room. The ratio of the volumes of the water m and M was then obtained by direct measurement instead of the ratio of the masses. The equation

$$L = \frac{v}{V} S(\theta_2 - \theta_1)$$

was used to calculate results. Over 150 experiments were made and the following table consists of eight consecutive experiments taken near the end of the list. The specific heat is taken at unity in the calculations and necessitates a correction for final results.

TABLE I.

θ_1	θ_2	θ_2-θ_1	v	V	L	P
17.04	93.52	76.48	7212	1027	537.07	761.4
17.71	92.93	75.22	8613	1207	536.76	756.7
21.75	97.15	75.40	14400	2021	537.23	781.4
14.21	91.17	76.96	29987	4293	537.57	770.2
25.16	98.72	73.56	13304	1819	538.01	753.7
15.39	98.21	82.82	11107	1709	538.25	746.1
11.60	90.32	78.72	10241	1497	538.52	741.2
17.73	82.10	64.37	9997	1193	539.40	759.4

When lower temperatures than those shown in the table were taken at the outlet, nearly all the steam was condensed. Radiation into the worm was great and the values of L obtained were very large. The condensed water was cooled below the temperature of condensation of steam and correct values of L could only be obtained by taking the temperature of the condensed water and substituting in equation

$$L = \frac{v}{V} S(\theta_2 - \theta_1) - (100^\circ - \theta_3)S.$$

The values thus obtained did not have the consistency in consecutive experiments that the other experiments possessed. If the results in the table are corrected to the nitrogen scale of temperature and for the variation in the specific heat of water between the required temperature limits, they approximate closely to Callender's standard value of 540.2 calories at 20° C. They average several points lower in value and point to the existence of a small constant error.

The results in the table were obtained directly from prime observations and compared very favorably with the best results by other methods, even though their measurements be made with the greatest degree of accuracy, and have all the necessary corrections. Thus Joly with the steam calorimeter in six experiments on the specific heat of water between 10° C. and 100° C. obtained results in which the measurements varied from 1.0044 to 1.0087. Barnes with the continuous electrical method obtained results in five experiments on the value of J, the mechanical equivalent of heat, at 29° C., which vary between the limits 4.1771 and 4.1803. These two methods are probably the most accurate heat methods known. The method of mixtures, with the greatest possible refinement in the measurements, may acquire the same degree of accuracy, but the corrections are too large and probably large constant errors exist. The continuous method of steam calorimetry as here outlined, is capable of a much greater refinement. The small constant error is probably due to the existence of air in the water and the subsequent production of bubbles in the outflowing water (m). The quantity of air is small and the heat absorbed in raising its temperature may be neglected. The existence of water vapor in these bubbles and the consequent loss of heat on account of the high latent heat of vaporization cannot be ignored. It probably fully accounts for the lower average value of the latent heat which was obtained. It probably also accounts for a portion of the difference in the values obtained, since its effect was irregular and depending on the temperature of the outflowing water.

An attempt to eliminate this source of error was only partially successful. The pressure on the water was raised, by raising the level of the outflow five or six feet and resulted in a diminution of the number and size of the bubbles. A number of experiments have been made with special care which have given concordant results in consecutive experiments which differ only in the fifth significant figure. The constant errors enter to a much greater extent and have not been as yet completely classified. An absolute determination of the latent heat of condensation of steam is being made with the greatest refinement and this paper is a preliminary one and intended simply as a development of the method.

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ON THE DIFFERENTIAL TELEPHONE.[1]

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By William Duane and Charles A. Lory.

1. The authors have tested the merits of a "differential telephone" as a means of measuring a self-inductance, and have devised an exceedingly accurate method of measurement. The differential principle has been used before in connection with a telephone,[2] but the accuracy claimed for it in the measurement of a self-inductance was only about one per cent. With the instrument described below an accuracy greater than one fiftieth of one per cent. has been attained.

2. A differential telephone receiver is one on the bobin (or bobins) of which two coils AA' and BB' (Fig. 1) are wound side by side. By suitable means these coils are adjusted so as to have equal self-inductances and equal resistances, and so that the magnetizing effect of a current flowing through one coil from A to A' is exactly annulled by that of an equal current flowing through the other coil from B to B'. A variable self-inductance standard S is joined in series with coil AA', and the coil of unknown self-inductance X in series with coil BB'. A non-inductive variable resistance R is inserted in series with S or X according as the resistance of X is greater or less than that of S. The two entire circuits are then joined in parallel and an alternating electromotive force is applied to the branch points C and D. By varying R and S values can be found easily such that no sound is heard in the receiver. When this is the case the two parallel currents must be

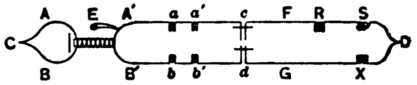

Fig. 1.

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[1] Presented at the St. Louis meeting of the American Association for the Advancement of Science, December, 1903.

[2] H. Ho, Electrical World and Engineer, May, 1903.

equal to, and in phase with each other, and therefore the self-inductance of X must equal that of S.

3. Before the instrument is ready for use, three adjustments are necessary, but these may be made once for all, and do not have to be repeated before each measurement.

First, the magnetic effects of the two receiver coils must be equalized. This is the most difficult adjustment, as it is impossible to wind the two coils exactly alike. The equality of the magnetic effects can be tested by joining the ends A' and B together, and sending an alternating current through the two coils in series in the direction $AA'BB'$. The same current then passes through each coil in the proper direction, and the magnetic effects are equal and opposed to each other, if no sound is heard in the receiver. In making the receiver it is best to wind the two coils side by each and as close together as possible, and each layer of turns should be evenly distributed. If in the first layer the turns belonging to coil AA' are nearer the diaphragm than those belonging to coil BB', in the second layer the positions of the turns belonging to the respective coils should be reversed, and so on alternately in the succeeding layers. Even with this careful winding the magnetic effects are not exactly equal to each other; in our instrument the difference between them amounted to the effect of a fraction of a single turn. A number of schemes for balancing the residual effect were tried, but the only one that completely extinguished the sound in the receiver was the insertion of a small coil E of about ten turns of wire in series with one of the receiver coils. E was mounted on the frame of the receiver in such a way that it could be shifted about with its plane always parallel to the common axis of the coils AA' and BB'. A position could be found for E that completely extinguished the sound, even though an alternating electromotive force of twenty volts was applied to the coils.

The second and third adjustments are the equalizations of the resistances and self-inductances of the coils. The self-inductances can be equalized by placing in series with each receiver coil a pair of coils (aa' and bb'), and by altering the distances between the coils in each pair. The resistances can be equalized by means of sliding contacts moving along pairs of parallel wires (c and d). The test for the equality of the resistances and of the self-inductances is accomplished by joining the circuits from A to F and from B to G in parallel, applying an alternating electromotive force to the branch points and varying the adjustments until no sound is heard in the receiver. After these adjustments have been made the instrument is ready for measurements.

4. In comparing the self-inductance of a coil X with that of a standard S two balances must be made. The resistance of the parallel circuits must be made equal to each other by varying R, and the self-inductances equal to each other by varying S. One of these balances does not depend upon the other (as is the case, for instance, in Maxwell's method of comparing a self-inductance with a capacity), and hence the double balance is much easier than it otherwise would be.

If the divisions of the resistance box R are not small enough, the final balance of the resistances may be made by means of the sliding contacts c and d.

Absolute silence in the telephone receiver can be obtained easily, if there is no iron in the self-inductance. With an iron core a very sharp minimum can be obtained, but not in general total silence. If, for instance, the coil X is a Morse telegraph sounder, several tones of different pitches can be heard, and values of S and R can be found that extinguish the most prominent tone.

5. The accuracy of the measurement may be estimated by means of the following calculation. Suppose that the resistance of the two parallel circuits are equal to each other and each equal to r, and further that the reactances of the two circuits differ from each other by the small amount dx, x being the reactance of one circuit and $x + dx$ that of the other. The complex expressions for the impedances of the two circuits are ($j = \sqrt{-1}$).

$$Z_1 = r + jx, \qquad \text{and} \qquad Z_2 = r + j(x + dx).$$

If e is the simple alternating electromotive force applied to the branch points C and D, and I_1 and I_2 are the currents in the two branches respectively,

$$I_1 = \frac{e}{r + jx}, \qquad \text{and} \qquad I_2 = \frac{e}{r + j(x + dx)}.$$

The sound heard in the receiver depends upon the difference between the two currents, and, if dI is this difference,

$$dI = I_1 - I_2 = e\left[\frac{1}{r + jx} - \frac{1}{r + j(x + dx)}\right].$$

Reducing to a common denominator, neglecting small quantities of higher orders than dx and eliminating the imaginary unit j, we find that the absolute magnitude of dI is

$$dI = \frac{edx}{r^2 + x^2}.$$

If dI is the smallest current that can be detected, when it flows through one of the receiver's coils, dx cannot be greater than

$$dx = (r^2 + x^2)\frac{dI}{e}.$$

To estimate the numerical value of the accuracy assume that the resistances r and the reactance x are each 50 ohms, that e is one volt and that a current of one millionth of an ampere can be detected by the telephone. These values are not unusual. Then

$$dx = \tfrac{1}{200}\text{ ohm},$$

and the percentage error is

$$100\frac{dx}{x} = \tfrac{1}{100}\text{ per cent.}$$

The reactance x may be taken to be that of the standard S alone, for the reactance of the rest of the branch circuit is very small. The reactance is due to self-inductance, and therefore the percentage error in the measurement of the self-inductance is also $\frac{1}{100}$ per cent.

As a matter of fact the accuracy does not fall far below the theoretical value. It is not difficult to measure a self-inductance to within one twentieth of one per cent., and with care the accuracy can be considerably increased.

6. Electrolytic resistances also may be measured by means of the differential telephone. For this purpose the coil X is replaced by a vessel with suitable electrodes and containing the electrolyte, and the standard S is removed.

7. The advantages of using a differential telephone as described above for measuring a self-inductance are: (*a*) that the apparatus is portable and does not get out of order easily; (*b*) that great accuracy can be attained and the manipulation is not difficult; (*c*) that the heating of the circuits by the currents does not alter the self-inductance balance, and therefore that large electromotive forces may be used; and (*d*) that only one standard is required; it is not necessary to know the values of any resistances or the lengths of a bridge wire. The disadvantage is that the self-inductance of the standard must equal that of the coil to be measured. If, however, the self-inductance to be measured is smaller than the smallest inductance obtainable in the standard, a fixed standard may be placed in series with the unknown coil, and the sum of their self-inductances measured; and if the self-inductance to be measured is greater than the greatest inductance obtainable in the standard, a fixed standard may be placed in series with the variable standard. Thus the range of measurement may be increased indefinitely beyond the limits of the variable standard.

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ON THE DETERMINATION OF REFRACTIVE INDICES BY MEANS OF CHANNELED SPECTRA.

By S. R. Williams.

If the light reflected from two parallel optical surfaces be examined with a spectroscope of sufficient resolving power, the resulting spectrum will be traversed by dark bands corresponding to those wave-lengths which interfere, the center of a dark band occurring when $2\mu D = 2N\lambda/2$ and the medium between the surfaces is of a less refractive index than that composing the optical surfaces. For the center of a light band $2\mu D = (2N + 1)\lambda/2$, where D is the linear thickness of the space intervening, λ the wave-length and N some intregal number. In case μ becomes equal to unity, as occurs when we have a vacuum, the value of N in the above equation may be derived, giving the length of the path D in wave-lengths of light. Using the sun as a source of light there will appear in the spectrum the Fraunhofer lines, in addition to the interference bands, thus furnishing a scale of reference for every interference band.

If two dark bands appear in determinate parts of the spectrum corresponding to wave-lengths λ_1 and λ_2, then by the above equations $2\mu_1 D = N\lambda_1$ for the longer wave-lengths, and $2\mu_2 D = (N + m)\lambda_2$ for the shorter, whence assuming $\mu = 1$ we obtain

$$N = \frac{m\lambda_2}{\lambda_1 - \lambda_2}.$$

A comparison of the results obtained by various investigators in the determination of refractive indices shows at once that the optical thickness cannot be obtained by the above formulæ for those substances in which μ is such an uncertain quantity.

Dr. D. B. Brace[1] has shown that the difference in path of two interfering rays, or the optical thickness, may be determined independently of the factor μ. His method is to take a cell, whose thickness can be varied, (usually a wedge-shaped cell) and if, in the variation of the thickness, m bands are shifted past a definite point in the spectrum for which the difference in path N is to be determined, and n is the ratio of the bands between two definite wavelengths, λ_1 and λ_2, before and after the variation in thickness, then

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[1] Phil. Mag. (48), 1899, p. 345; (1), 1901, p. 339.

$$N = \frac{mn}{1 - n}.$$

Being able to determine the difference in path thus, we are furnished with the means for determining the value of μ for any transparent substance. For, if we take as a medium of reference a substance of index μ_r, which is accurately known, $2\mu_r D = N_r \lambda$. In the body whose index is to be determined, $2\mu_e D = N_e \lambda$. D and λ being made the same, we have

$$\mu_e = \frac{N_e}{N_r} \mu_r,$$

that is, the refractive index of any substance is equal to the ratio of the optical lengths of equivalent paths in that substance, and the medium taken as a reference, multiplied by the index of the reference film.

For liquids the path D may be easily made the same by making a thin wedge-shaped cell with its sides parallel, and allowing the light to be reflected from a narrow vertical section of the same. If the upper half of the narrow section reflects from the surfaces of the film taken as a reference, and the lower half from a substance whose index is to be determined, there will occur in the spectrum, simultaneously, two sets of interference bands from which the orders of interference may be calculated, and from these the index.

By the distribution of the two sets of bands thus obtained, the dispersive power of the two substances may be compared, for if μ was larger in one than in the other, the bands would appear more frequent throughout the spectrum as shown by our equation above. In this way the complete record of dispersion of a body may be obtained throughout the spectrum. Furthermore the bands superimposed upon the Fraunhofer lines as a scale may be photographed, and a permanent record made of the dispersion of the substance examined.

To make this a practical working method was the object of this investigation.

A four-inch Rowland concave grating, 14,438 lines to the inch, with Brashear mounting, and focal length of ten feet was used. Fig. 1 shows the arrangement of the optical system. The slit was illuminated by the direct rays of the sun, and an image of the same was formed on the wedge *W* by the lens *L*. In the usual mounting of the Rowland concave grating, the slit or its image should be

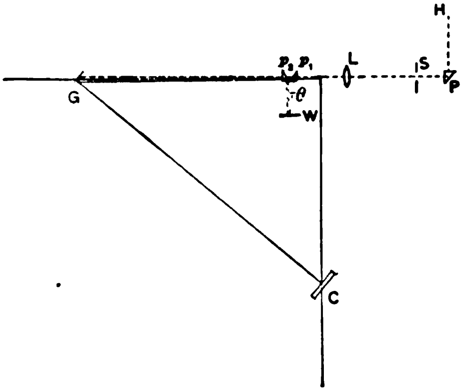

Fig. 1.

placed over the intersection of the ways, in order that the spectrum may be brought to a focus on the proper focal curve. Instead of doing this the light coming from the slit *S* through the lens *L* was reflected by means of the prism p_1 upon the wedge *W*, where the image of the slit was formed. The two surfaces of *W* returned the light to the prism p_2, which reflected it upon the grating *G*. The distance of *W* from p_1 and p_2 was such, that the image in p_2 was at the intersection of the ways, and thus the conditions for accurate focusing were secured. The image of the slit at *W* served two purposes, in that it brought the Franuhofer lines and interference bands into focus at the same time, and also afforded the means of getting a narrow vertical section of the cell.

Plate glass cut in strips, 3 x 13 cm., and 6 mm. thick, formed the sides of the wedge-shaped cell. To keep the plates apart and also form the bottom and ends of the cell as well as the dividing strip between the films, cork strips about .75 mm. thick were cut out, as shown in Fig. 2. The plates were then held firmly against this strip by means of clamps, those on one end being screwed down more tightly than the other, in order to make the cell wedge-shaped. The mounting of the cell was so arranged by means of a rack and pinion, that it could be raised and lowered in a vertical direction, and also moved in the direction of its length, by means of a micrometer screw. For photographing the two sets of bands simultaneously the cell was so moved that the image of the slit occupied a position as *ab* in Fig. 2.

ABCD is that part of the cell containing the film of reference, while the rest of the cell holds the liquid whose index is to be determined. The two sets of bands having been photographed together the cell was moved parallel to its length, while the bands from the liquid film were counted as they moved past some fixed point in the spectrum, until the image of the slit occupied a position as *cd* in Fig. 2. In this position a set of bands throughout the spectrum was photographed, and knowing the index for one wave-length, it could be determined for all others by counting the bands.

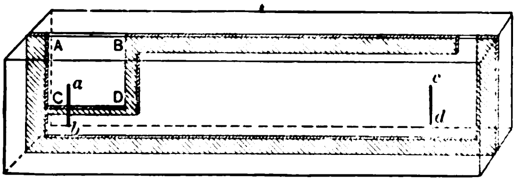

Fig. 2.

Air was used for a reference film. Its index has been very accurately determined, by means of the interferometer, and the presence of a vapor does not effect it, as it has been ascertained that the refractive index of dry air is only about one millionth greater than air saturated with a vapor. The values as found by various investigators, vary by little over one part in a million. Air has also been used as a medium of reference by other investigators, and so is used in this work.

The direction of variation in thickness of the cell is at right angles to the interference bands, since along their length, the thickness must be uniform. They will be parallel to the Fraunhofer lines then, when the refracting edge of the cell is parallel to the image of the slit. This was the means used for getting the plates of the cell, parallel in a vertical direction, for, if the interference bands were brought into coincidence above and below the dividing strip, before the liquid is introduced, the value of D for both films must be the same.

Another condition necessary, to give D an equivalent path, in both films, is, that the incidence be normal upon their surfaces, for, owing to refraction at the bounding surfaces the ray will be bent more or less for one than the other depending upon the difference in index, consequently D would vary for the two films. In the system used, normal incidence was not possible, but it was made so small, that it entered no appreciable error. Let AO, Fig. 3, represent the path of normal incidence upon air film xy

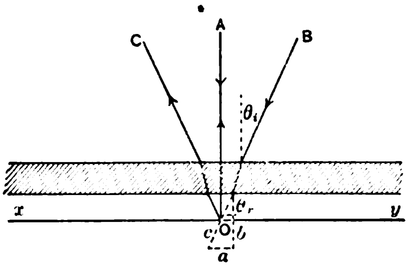

Fig. 3.

contained between two plates. Let BOC be the path of a ray at an incident angle of θ_i. Since the film xy is an air film, the angle of refraction at its surface will be the same as the angle of incidence on the plate ($\theta_i = \theta_r$). θ_r will also be a maximum for air, hence if it can be shown that the angle θ_r does not produce an appreciable error in difference between c and b, which are the lengths of D at normal and oblique incidence, then it can be shown that for a ray incident at an angle θ_i upon two films, as an air and a liquid film, the difference in D for the two is not an appreciable error. For the difference in the angle of refraction at the surfaces of the two films, can never be as large as θ_r, consequently the difference in length can never be as great as $c - b$ in the figure.

$$\tan \theta_r = \frac{a}{b}$$

$$\sin \theta_r = \frac{a}{c}$$

$$c - b = a\left(\frac{1}{\sin \theta_r} - \frac{1}{\tan \theta_r}\right)$$

$$\frac{c-b}{b} = \tan \theta_r\left(\frac{1}{\sin \theta_r} - \frac{1}{\tan \theta_r}\right) = \sec \theta_r - 1$$

but $(c - b)/b$ is the per cent. of error introduced. In the apparatus as set up, the light at prism p_1, Fig. 1, was diaphragmed so that θ_r was about 25′. Substituting this value in the above equation, shows an error of about three parts in a hundred thousand. With light incident on two films the error due to difference of path *D* is still less, as shown above.

In the liquid films with oblique incidence, dispersion produces a variation in *D* for the different wave-lengths, so that if the index of the substance under examination be smaller than that of the containing cells, the path *D* for the violet ray, will be greater than that of the red, since it will be bent away from the normal more than the less refrangible wave-lengths. We have shown that difference in path, due to refraction, produced a negligible error, and since the angle of deviation is always less than the angle of refraction, no error in difference of *D* for the various wave frequencies will occur.

Again the length of *D*, as determined from the bands in the photographs, will be augmented by change of phase, at reflection from the bounding surfaces of the film, if the conditions of reflection for the two beams are not the same. In order to increase the intensity of light in reflection from the surfaces, a full silvered surface was used at the back. After repeated trials, it was found that an approximate half silvered front surface, which gave a brighter image of a flame by reflection, than by transmission, product the blackest bands in the channeled spectra.

O. Wiener[1] has found that the change of phase by reflection, varies with the thickness of the silvering, increasing as a retardation from 0 to $3/4\lambda$, for all wave-lengths, as the thickness of silver increased from zero to a full silver.

[1] Wied. Annal. (31), 1887, p. 647.

The index of silver is about .25, so that in the cell that was used, if the half silvering was placed on the rear surface of the front plate, and the full silvering on the front surface of the rear plate, then for both films, the condition of reflecting from a less refracting substance to a greater, was secured for the two interfering rays.

According to Wiener, the half-silvered surface introduced a retardation of about $\lambda/2$, while at the rear surface it was $3\lambda/4$. This made the difference in phase of the two interfering rays, greater by about $\lambda/4$, since the ray reflected from the back surface has been retarded that much more than the one reflected from the front surface. With the order of interference that was used in this work, this entered an error of less than three parts in one hundred thousand in determining the order.

In making the computation of indices, this change of phase was not regarded, and since in photographing, the bands from the two films were brought into coincidence with the D_1 line, the orders of interference for these were regarded as an odd multiple of $\lambda_D/2$.

$$(2N + 1)\frac{\lambda}{2} = 2\mu D$$

then becomes the formulæ for finding the order of an interference band.

The cell was housed in a pasteboard box, which kept the temperature uniform during the photographing, so that the bands did not shift due to that cause. The temperature was taken at the beginning of the series of photographs, and is indicated on the plates.

At times, a shift of the bands did occur, but this was due to a yielding of the cork strip between the plates, or other mechanical effects. It was found that if the cell was allowed to stand before using, no difficulty was encountered from this source, for an eye piece was attached to the side of the camera box, whose focus was on the focal curve of the grating, and through this the bands were watched to see that they did not shift with respect to the Fraunhofer lines.

Mitchell has shown that the astigmatism of a grating depends upon the length of the illuminated portion of the slit, the length of the ruled lines, and the angle which the incident light makes with the axis of the grating. On account of this property, comparison work is not possible as in the prismatic spectrum. In photographing the two sets of bands, comparison work was done, but other conditions were introduced that do not occur in ordinary comparison work. The light falling upon a grating was slightly divergent, and the dividing strip in the cell, cut out a narrow section of light across the middle of the ruled portion of the grating. The light above this dark strip came from one film, and that below from the other. The length of ruling that was producing the spectrum for one set of bands, was therefore less than half the actual length of ruling of the grating, and as a result the interference bands, from one film, extended about half the width of the spectrum.

If D is the thickness, μ the index, λ the wave-length, and N is the order of interference, the distribution of the bands throughout the spectrum is represented by the equations:

$$(1) \qquad N = \frac{2\mu D}{\lambda}$$

$$(2) \qquad N = \frac{2D}{\lambda} \text{ where } \mu = 1, \text{ as for a vacuum.}$$

Differentiating these we have,

$$(3) \qquad \frac{dN}{-d\lambda} = \frac{2D}{\lambda^2}\left(\mu + \lambda\frac{d\mu}{-d\lambda}\right),$$

$$(4) \qquad \frac{dN}{-d\lambda} = \frac{2D}{\lambda^2}.$$

Equations (1) and (2) are the equations of an equilateral hyperbola, N and λ being the variable parameters. In (3) and (4) the left hand side of the equation, represents the number of bands between wave-lengths λ and $\lambda - \delta\lambda$, and is expressed on the right hand side in terms of D, λ and μ. The variation of the order with wave-lengths in the two equations, (3) and (4), differ by the factor in parenthesis which expresses the difference in variation between the two sets of bands. Since in the two equations $2D/\lambda^2$ appears, which is the expression for the variation of order due to wave-length alone, if we superimpose a set of bands, *e. g.*, those in a vacuum,

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[1] J. Hopkins, Univ. Circulars, June, 1898.

whose variation is represented by (4), upon a set of bands represented by (3), the differential effect will be that due to the dispersion of the substance whose bands are represented by (3). To do this, the bands from the two films are brought into coincidence, say in the less refrangible portion of the spectrum. If now we go toward the violet, the bands in the spectrum whose variation is represented by (3) will, in general, increase in number more rapidly than those used as a scale. Consequently they will get out of coincidence. If then they should come into coincidence again, due to the bands not increasing so rapidly as those on the scale, the term in parenthesis must diminish, which indicates anomalous dispersion. In a subsequent paper, it will be shown more in detail how this method may be used for the detection of this characteristic.

Preliminary work has been done in adapting this method to the determination of refractive indices of solids. The optical system was, in general, the same as used in working with liquids. The difficulty with solid wedges, is to get a reflecting surface for the wedge and an equivalent film of air. If silvered plates be placed on both sides of the solid wedge, as for the liquid film, it is impossible to get the plates in close enough contact to the wedge, so as not to have thin air films intervening. This difficulty was overcome, by measuring these air films, and thereby obtaining the equivalent film of air for reference. In Fig. 4 is shown a vertical cross section of the cell used in getting the order of interference in the wedge and an equivalent film of air. *W* is the solid wedge between two glass plates, silvered as they were in the liquid cell described above. The path of the light at *A* gives the total thickness of air space, *B* that of the wedge and air films on both sides. By properly silvering the lower part of the wedge, the interference bands due to the wedge itself, may be obtained in *C*. $B - C$ gives the thickness of the air films on the two sides of the wedge. $A - (B - C)$ gives the thickness of an air film equivalent to the wedge. Consequently $C/[A - (B - C)]$ gives the index as compared with air. It was impossible to get the three sets of bands simultaneously, but *A* and *B* were first obtained and photographed, and then by means of rack and pinion, the cell was raised and *B* and *C* obtained.

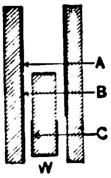

Fig. 4.

With proper adjustments, there was no shift of the bands in raising the cell vertically, since its sides and that of the wedge are parallel in that direction.

In solids showing double refraction, the optical system was arranged as shown in Fig. 5, with a nicol, *A*, before the slit and another one, *E*, between the prism p_2 and the grating.

If a ray of light, polarized at an angle of 45° to the principal axis of a crystalline wedge, pass normally through and is reflected back again, the emergent light, when resolved by a spectroscope,

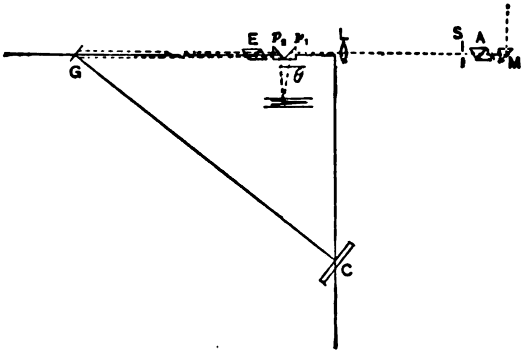

Fig. 5.

will be traversed by interference bands due to double refraction in addition to the ordinary bands arising from the wedge. The superposition of the two sets of these latter bands, give rise to a maximum and a minimum in the intensity, producing the bands from double refraction referred to. The formulæ for these minima, when the nicols are crossed, is $N = 2D[(\mu_e - \mu_0)]/\lambda$. In this way both the bands due to interference between the beams reflected between the front and back surface, and those due to differential double refraction may be photographed.

With double refracting crystals, the system of reflection at p_1 and p_2 had to be changed, and is shown in Fig. 6. In using the prisms p_1 and p_2 only, there would be a change of phase between the component vibrations. By using a double system of reflection, at right angles to each other, as shown in the cut, the two components will have practically the same change of phase introduced. This double reflection will place the image of the slit in a horizontal position, which necessitates turning the wedge so that its length is at right angles to the image of the slit.

Plate I. is a series of photographs for triple-distilled water. The photographs are arranged with the shorter wave-lengths to the left. In each set of photographs, No. 4 was the first setting made in the spectrum, and is that of the liquid and air bands together, between the Fraunhofer lines, β_2 and D_1. No. 3 was taken in the same portion of the spectrum, after shifting several hundred bands. The others were taken in the order 5, 6, 2, 1.

In Plate I. the number of air bands between β_2 and D_1 is 276.6 from which the order 1978.5 for the Fraunhofer line D_1 is obtained by the formulæ

$$N = \frac{m\lambda_2}{\lambda_1 - \lambda_2}.$$

In the liquid bands there are 374.7 between these two wave-lengths, and after shifting 338 bands past the D_1 line in the spectrum and photographing again, there are by count 326.7 bands in this same region, substituting these values in our equation

$$N = \frac{mn}{1 - n} = \frac{338 \times \frac{326.7}{374.7}}{\frac{48}{374.7}} = 2300.5.$$

The order as found for the liquid is that of the D_1 line in photograph No. 3. For the D_1 line in No. 4 we add 338 to 2300.5 = 2638.5. The ratio between these two orders,

$$\frac{N \text{ liquid}}{N \text{ air}} = \mu = \frac{2638.5}{1978.5} = 1.3336.$$

For the D_1 line in No. 3, the order for air would be the order for liquid at that point, divided by the index,

$$\frac{2300.5}{1.3336} = 1725.0.$$

From these two orders of air and liquid for the D_1 line, the orders for all other points in the spectrum may be calculated and counted from the photographs.

In counting the bands, they were laid on a dividing engine under a micrometer eye piece, and as the photographs were shifted under the cross wires, the bands were counted. The fractional part of a band being estimated only to tenths.

The results from all of the photographs shown, were obtained in the manner described above, and are tabulated below.

Plate I.

Triple-distilled Water. $m = 338$. *Temp.* 22°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674×10^{-5}	1480.9	1971.1	1.3310
6.5630 " "	1549.9	2063.8	1.3316
5.8961 " "	1725.0	2300.5	1.3336
5.6169 " "	1810.7	2416.9	1.3348
5.3283 " "	1908.7	2549.2	1.3356
5.2270 " "	1945.8	2599.4	1.3359
5.1728 " "	1966.2	2627.4	1.3363
4.9577 " "	2051.4	2743.8	1.3375
4.8615 " "	2092.1	2799.4	1.3381
4.6680 " "	2178.7	2917.6	1.3391
4.3837 " "	2320.1	3111.0	1.3409
4.2269 " "	2406.2	3228.5	1.3417
4.1019 " "	2479.5	3330.5	1.3432
3.9686 " "	2562.6	3445.0	1.3443

Plate II.

Absolute Alcohol. $m = 393$. *Temp.* 22°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674×10^{-5}	1268.0	1721.0	1.3572
6.5630 " "	1326.4	1802.1	1.3586
5.8961 " "	1476.2	2009.5	1.3612
5.6169 " "	1549.5	2111.5	1.3627
5.3283 " "	1633.4	2227.5	1.3637
5.2270 " "	1665.1	2271.5	1.3642
5.1728 " "	1682.5	2296.0	1.3646
4.9577 " "	1755.5	2397.7	1.3655
4.8615 " "	1790.3	2446.3	1.3664
4.6680 " "	1864.4	2550.4	1.3679
4.3837 " "	1985.5	2721.3	1.3705
4.2269 " "	2059.1	2825.1	1.3720
4.1019 " "	2121.9	2913.5	1.3731
3.9686 " "	2193.0	3014.5	1.3746

Plate III.

a-Monobromonapthalin. $m = 475$. *Temp.* 24°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674 × 10^{-5}	1440.1	2374.0	1.6485
6.5630 " "	1507.2	2489.2	1.6515
5.8961 " "	1677.5	2787.5	1.6617
5.6169 " "	1760.9	2934.6	1.6665
5.3283 " "	1856.2	3103.6	1.6720
5.2270 " "	1892.2	3168.2	1.6743
5.1728 " "	1911.0	3204.1	1.6767
4.9577 " "	1994.9	3354.9	1.6817
4.8615 " "	2034.5	3427.5	1.6847
4.6680 " "	2118.7	3584.6	1.6918
4.3837 " "	2256.2	3844.7	1.7034
4.2269 " "	2339.5	4007.6	1.7130
4.1019 " "	2411.2	4149.7	1.7210
3.9686 " "	2492.1	4322.5	1.7345

One of the difficulties met with in this method, is the shifting of the bands during the photographing as occurs in all interference work. This was mechanical, and was overcome by shifting the cell, for all the shift of the bands, with respect to the Fraunhofer lines, originated in the cell itself. That the Fraunhofer lines and

Plate IV.

Oil of Cinnamon (*Cassia*). $m = 273$. *Temp.* 25.5°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674 × 10^{-5}	1229.0	1919.1	1.5615
6.5630 " "	1286.3	2014.2	1.5659
5.8961 " "	1431.6	2257.5	1.5769
5.6169 " "	1502.7	2379.3	1.5833
5.3283 " "	1584.0	2519.0	1.5903
5.2270 " "	1614.8	2572.5	1.5937
5.1728 " "	1631.7	2602.4	1.5949
4.9577 " "	1702.4	2728.0	1.6024
4.8615 " "	1736.2	2788.5	1.6061
4.6680 " "	1808.1	2920.0	1.6149
4.3837 " "	1925.5	3141.0	1.6312
4.2269 " "	1997.0	3283.5	1.6437
4.1019 " "	Absorption, no bands visible.		
3.9686 " "	" " " "		

PLATE V.

Benzole. $m = 235$. *Temp.* 22°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674×10^{-5}	1298.7	1924.9	1.4822
6.5630 " "	1359.2	2017.7	1.4844
5.8961 " "	1512.8	2254.4	1.4902
5.6169 " "	1588.0	2371.6	1.4934
5.3283 " "	1673.9	2505.4	1.4967
5.2270 " "	1706.4	2556.4	1.4981
5.1728 " "	1724.3	2584.4	1.4988
4.9577 " "	1799.0	2702.5	1.5022
4.8615 " "	1834.7	2758.9	1.5037
4.6680 " "	1910.6	2880.4	1.5076
4.3837 " "	2034.7	3079.4	1.5134
4.2269 " "	2110.2	3202.8	1.5177
4.1019 " "	2174.5	3308.4	1.5214
3.9686 " "	2247.4	3429.4	1.5259

interference bands appear simultaneously, is one of the important features of this method. No matter what apparatus is used, the scale of the Fraunhofer lines will always be the same, from which the measurements are made, and no mechanical errors can enter. The shift of bands which might arise due to changes of temperature, must be guarded against in all methods.

PLATE VI.

Olive Oil. $m = 267$. *Temp.* 26°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674×10^{-5}	1190.3	1721.0	1.4458
6.5630 " "	1245.7	1802.1	1.4474
5.8961 " "	1386.5	2012.5	1.4514
5.6169 " "	1455.4	2116.5	1.4542
5.3283 " "	1534.2	2234.5	1.4565
5.2270 " "	1564.0	2279.5	1.4567
5.1728 " "	1580.3	2304.2	1.4581
4.9577 " "	1648.8	2407.6	1.4602
4.8615 " "	1681.5	2457.5	1.4615
4.6680 " "	1751.1	2563.5	1.4639
4.3837 " "	1864.9	2733.0	1.4655
4.2269 " "	1934.0	2839.5	1.4682
4.1019 " "	1992.9	2930.6	1.4705
3.9686 " "	2059.8	3034.5	1.4732

It is also possible with the normal spectrum, to determine directly the index for any wave-length. In the prism method, we are dependent upon the more prominent Fraunhofer lines, for points of reference.

In conclusion, the author desires to express his thanks to Professor Brace for valuable assistance rendered him, whereby he was enabled to carry out this research.

Physical Laboratory,
University of Nebraska, June, 1903.

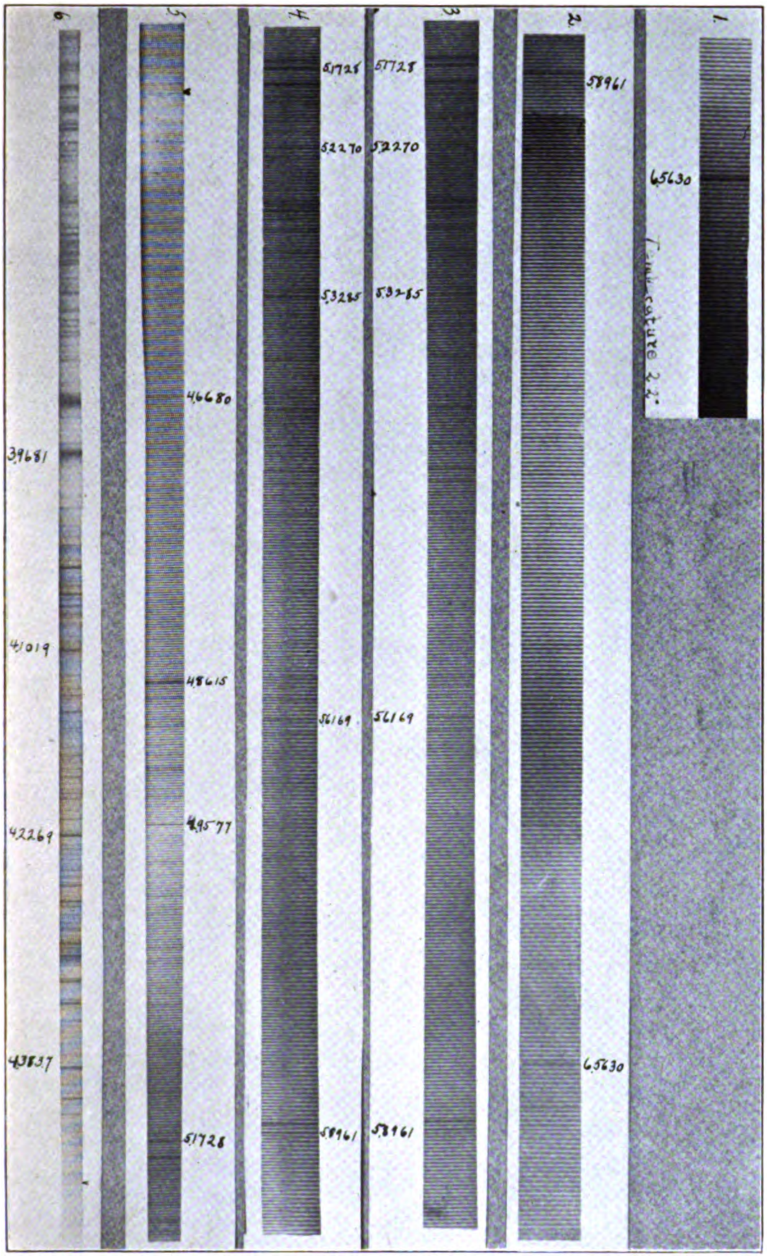

Plate I.

S. R. WILLIAMS

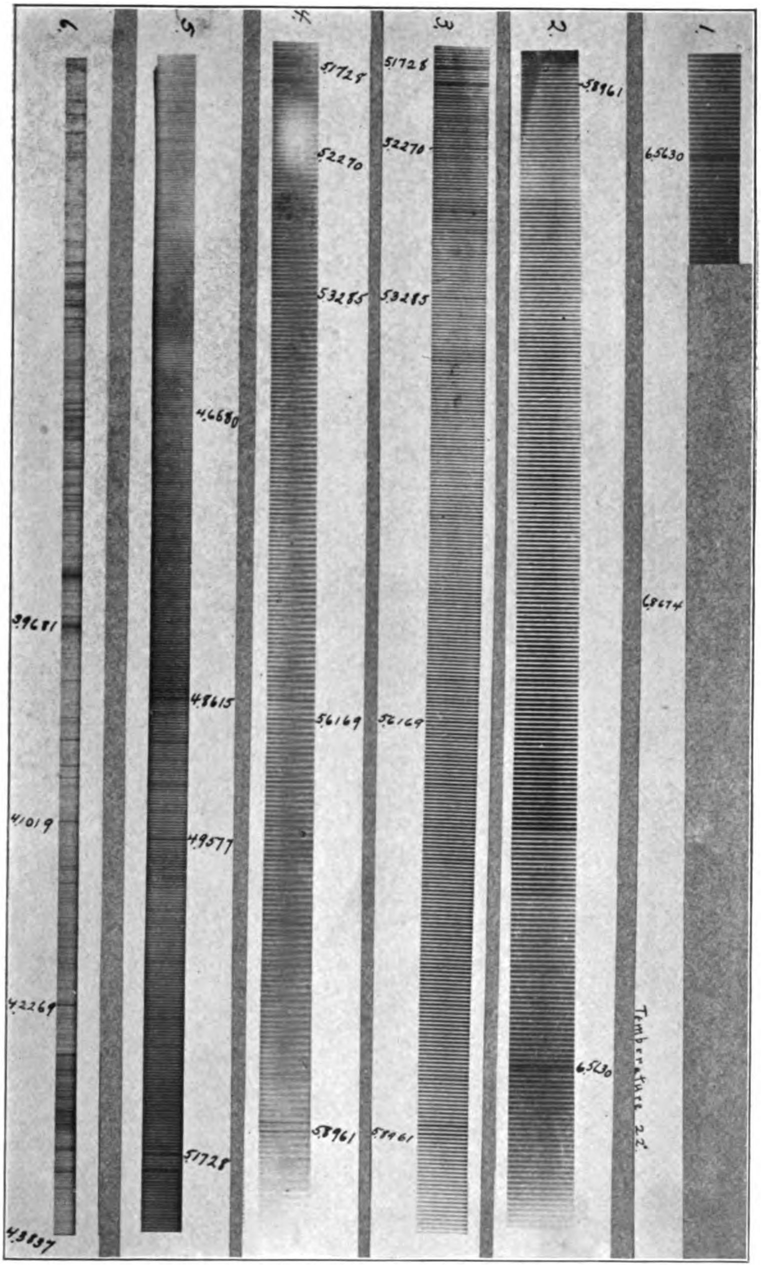

Plate II.

S. R. WILLIAMS.

PHYSICAL REVIEW, XCVII.
(To face page 294.)

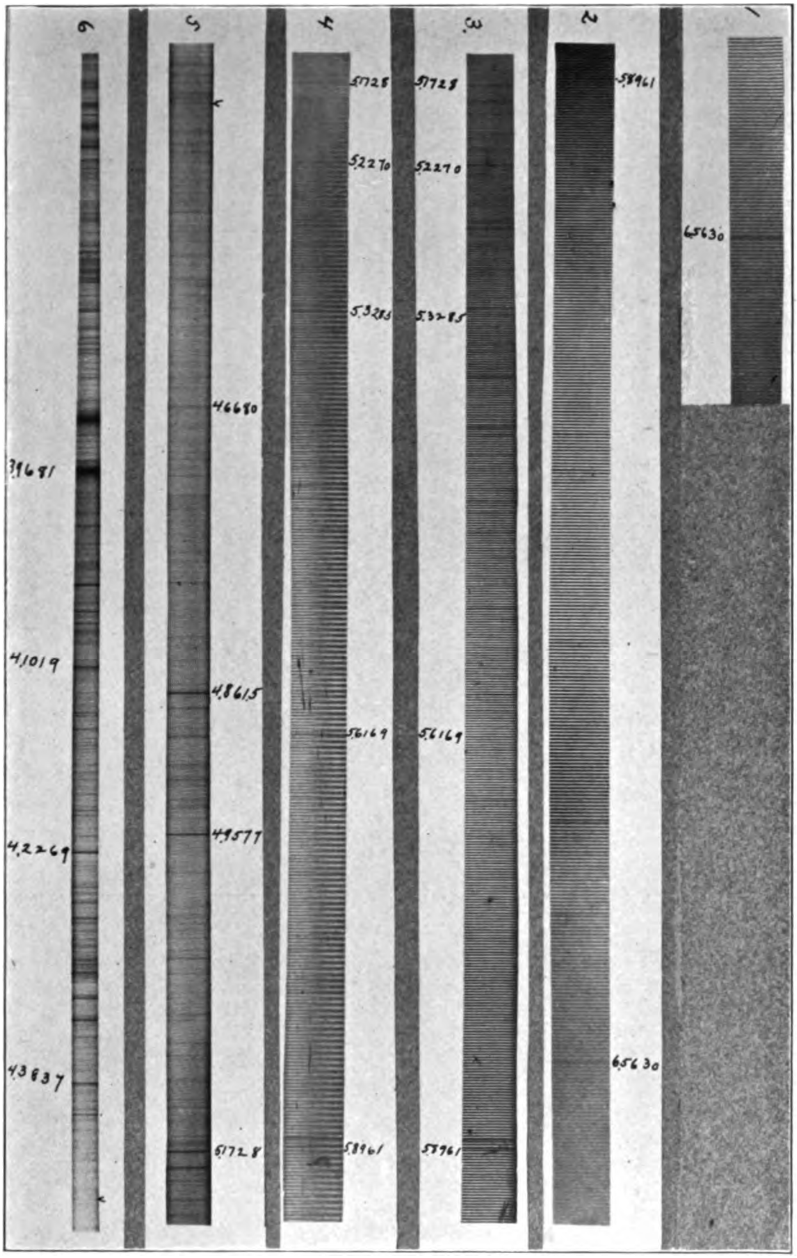

Plate III.

S. R. WILLIAMS.

PHYSICAL REVIEW, XCVII.
(To face page 294.)

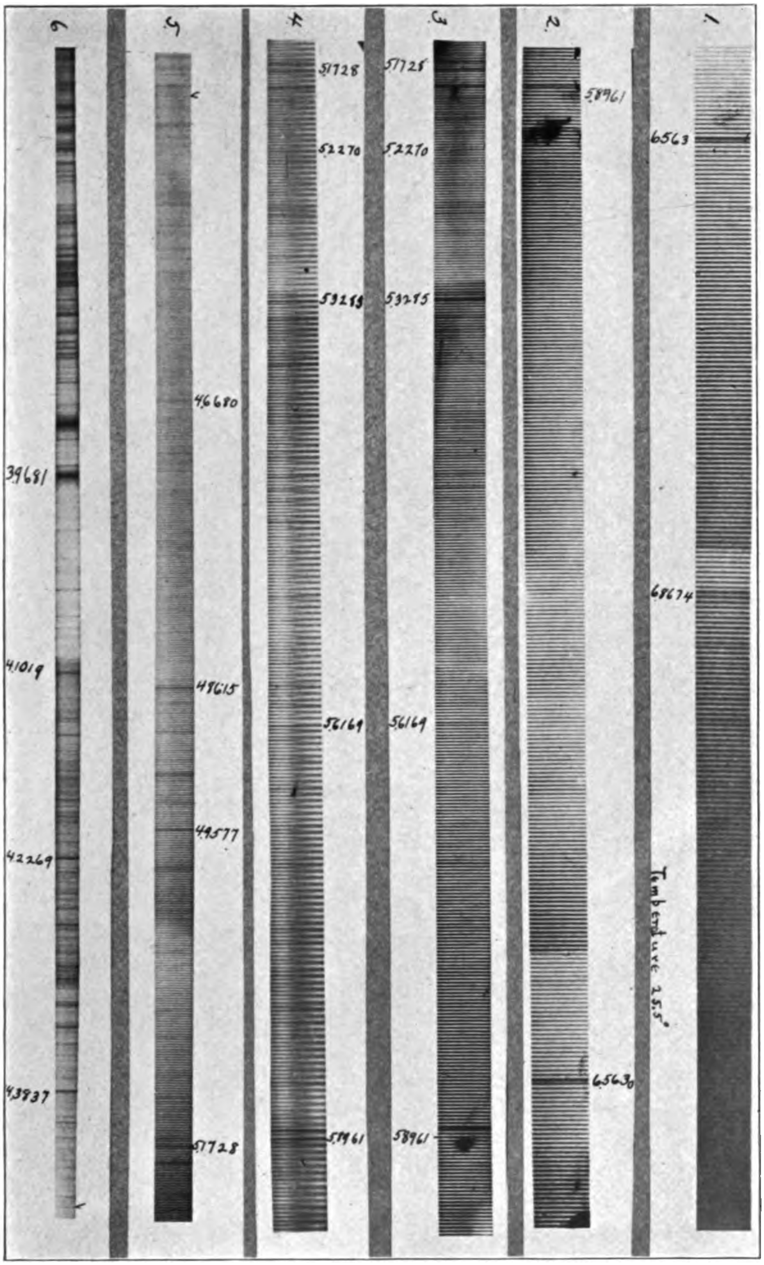

Plate IV.
S. R. WILLIAMS.

PHYSICAL REVIEW, XCVII.
(To face page 294.)

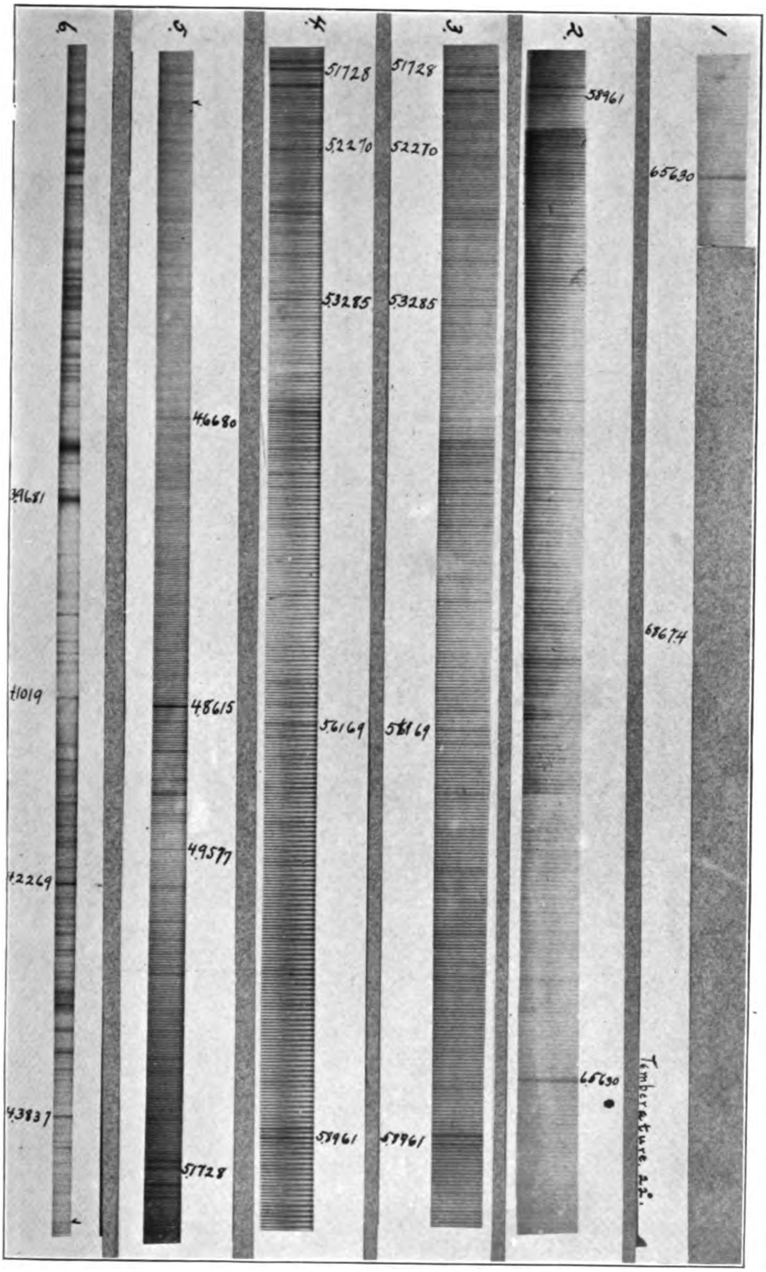

Plate V.

S. R. WILLIAMS.

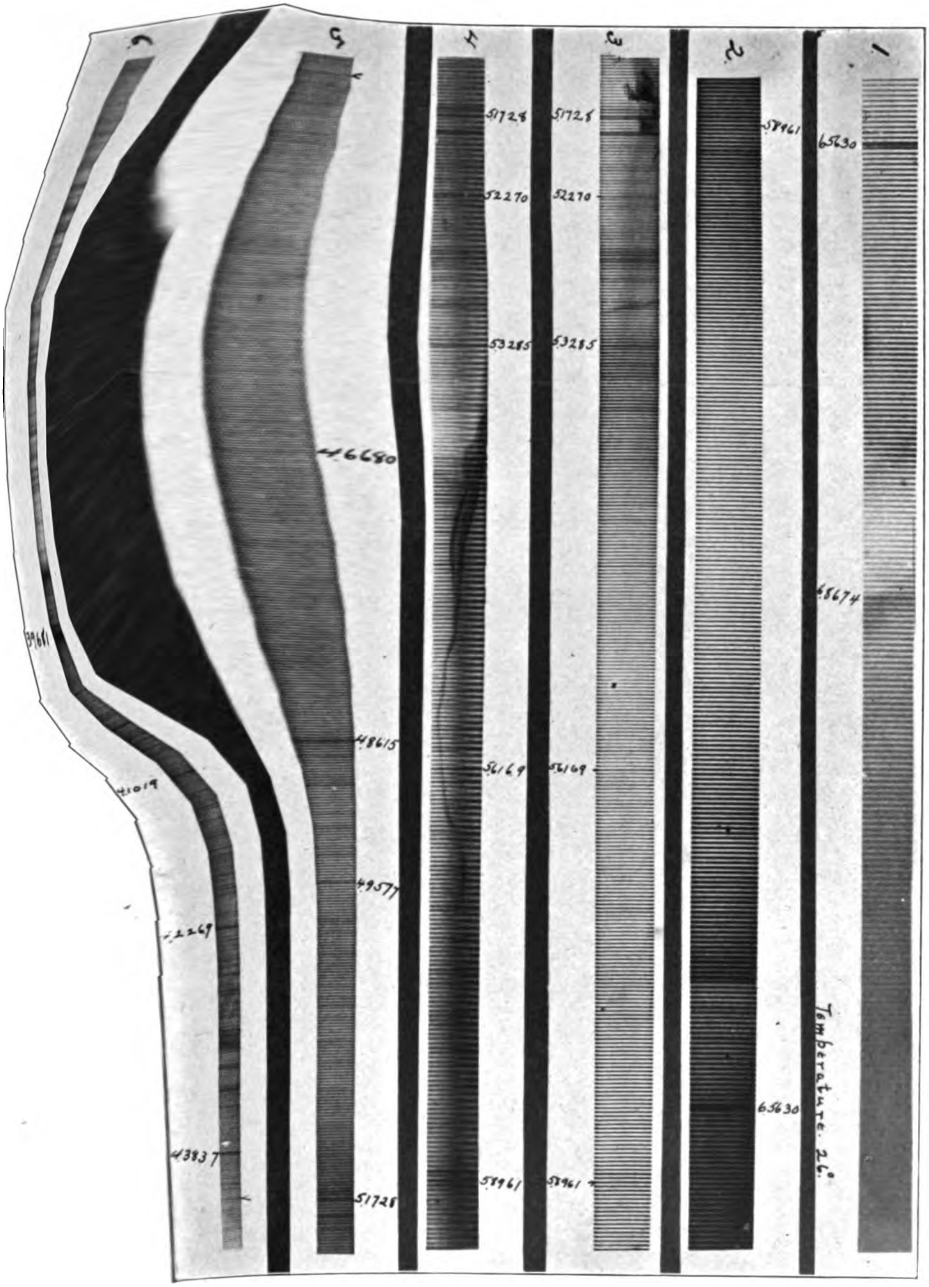

PLATE VI.

S. R. WILLIAMS.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE TWENTY-THIRD MEETING.

A REGULAR meeting of the Physical Society was held at Columbia University, New York City, on Saturday, February 27, 1904.

At the afternoon session the presidential address was delivered by President A. G. Webster, the subject being:

Some Practical Aspects of the Relations between Physics and Mathematics.

During the presidential address the American Mathematical Society met with the Physical Society in joint session.

The following papers were read:

1. The Conduction of Electricity in Mercury Vapor. A. P. WILLS.

2. Exhibition of Experiments Illustrating the Action of a Magnet on the Mercury Arc. PETER COPPER HEWITT.

3. Photography of Cloud Particles and the Photographic Record of Atmospheric Nucleation. CARL BARUS.

4. Preliminary Measurements of the Short Wave-lengths Discovered by Schumann. THEODORE LYMAN.

5. The Hall Effect in the Electric Arc. C. D. CHILD.

6. Note on Some Further Observations on the Radiation Produced in an Alternating Condenser Field. FERNANDO SANFORD.

Certain amendments to Articles I. and II. of the by-laws of the society, duly recommended by the Council, were on motion adopted. The purpose of these amendments was (1) to make it possible to elect Associate Members of the society hereafter as well as Regular Members; (2) to establish, for Regular Members, an entrance fee. Articles I. and II., as amended, read as follows:

I.

(*a*) The membership of the society shall consist of regular members, honorary members, and associate members.

(*b*) For the election of a new member to the society, either regular, honorary, or associate, or for the transfer of an associate member to regular membership, it shall be necessary that a proposition in due form signed by two members of the society shall be presented at a meeting of the council, and that at a subsequent meeting of the council the person named in such proposition shall receive the favorable ballots of a majority of the members present.

(*c*) Associate members are entitled to all the privileges of regular members except that they may not vote nor hold office.

II.

(*a*) The annual dues of regular and associate members shall be five dollars payable on the 1st of January. Each new regular or associate member, if elected before July 1, shall pay the full dues for the year; if elected after July 1, he shall pay two dollars and a half for the half year. Should the annual dues of any member remain unpaid beyond a reasonable time, the council shall remove his name from the list of members, after due notice.

(*b*) Newly elected regular members, or members transferred from associate to regular membership, shall pay an entrance fee of three dollars.

The following announcement was made by the secretary regarding the spring meeting of the Society:

The spring meeting will be held in Washington, D. C., on Friday, April 22, and Saturday, April 23, 1904. Sessions for the presentation of papers will be held on Friday from 2 P. M. to 5 P. M., and on Saturday from 10 A. M. to 1 P. M. On Friday at 6 P. M. there will be an informal dinner, and later in the evening a lecture upon a subject to be announced later. On Saturday, at 1 P. M., a luncheon by the Philosophical Society of Washington, complimentary to the Physical Society. Saturday afternoon an excursion to the Bureau of Standards and the Weather Bureau. The arrangement of further details regarding the meeting is in the hands of a committee of the Philosophical Society of Washington, at whose invitation the meeting is held in that city.

Circulars giving further information will be mailed to all members well in advance of the meeting.

ERNEST MERRITT,
Secretary.

SOME PRACTICAL ASPECTS OF THE RELATIONS BETWEEN PHYSICS AND MATHEMATICS.[1]

✓

BY ARTHUR G. WEBSTER.

IT is now more than four years since the American Physical Society has had a presidential address, and the only one that it has had set a pitch of ideality and enthusiasm that is hardly to be expected of subsequent addresses. I shall therefore crave your indulgence if I am not able to touch so varied a field, nor to soar on eagle's pinions as did our illustrious first president on that occasion, while I invite your attention to "Some Practical Aspects of the Relations between Physics and Mathematics."

Before touching upon my specific subject, however, it is proper to briefly review some of the chief happenings in physics between that time and this. Our own society was then making its entrance into the arena, and counted a membership of only 69, while now it is a strong and flourishing organization, embracing with few exceptions every working physicist in the country, and with a membership roll of 220. This number has not been attained by making membership open to every applicant, but the attempt has been made to limit it to persons who have actually made contributions to the science. In order to extend the privileges of the society to a wider circle of those who have an interest in physics, but have not yet been able to engage in productive research, the establishment of an associate membership is now contemplated.

Our first sad duty is to take account of our losses, chief among which is that of our first president, whose many-sided experimental skill and keen insight into the secrets of nature's ways made him without a peer among us. Who among us does not feel a patriotic pride when Rowland's value of the mechanical equivalent of heat is always quoted as among the most accurate, or when we remember that for the possibility of the most accurate work on the spectrum the world was indebted to an American? The breadth of Rowland's mind and the high ideals which ever guided him in the pursuit of truth are reflected in his presidential address, which marks a red-letter day in the history of this society.

Within the year physics in this country has suffered a loss of the most grave nature. Though he was not a member of this society, in the death of Josiah Willard Gibbs we all regret the loss of a master in a field to which we have as yet contributed but little to the world, the domain of theoretical or mathematical physics. To this subject Gibbs was what Rowland was to experimental physics. It is deeply to be regretted that his extreme modesty, and the very abstract nature of the subjects with which he dealt, prevented the knowledge of his work from being widely disseminated until late in his carreer, while his power to inspire and influence research might under other circumstances have been so much greater. Gibbs's chief title to fame will undoubtedly be found in his thermodynamical writings. Beginning with two important papers on geometrical methods of representation of the thermodynamical properties of bodies, by which in particular their behavior in the different states of aggregation was clearly exhibited to the eye, he showed the advantage of considering the entropy and energy of the substance as the independent variables determining its state rather than the temperature and pressure.

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[1] Presidential Address, delivered at a joint session of the American Physical Society and the American Mathematical Society, February 27, 1904.

The laws of thermodynamics, as developed by Clausius and the other classical writers, are two: First, the principle of equivalence of work and heat which says that if a system be taken through any closed cycle of transformations of its state, the total heat given to the system $\int dQ$ is equal to the amount of work $\int dW$ done by it on external systems. If instead of a cycle we consider an infinitesimal transformation, dQ and dW are not exact differentials of any function of the variables determining the state of the system, but the principle of equivalence states that their difference is, so that

$$(1) \qquad dQ - dW = dU,$$

U being a function of the state of the system, called its energy. Secondly, although dQ is not an exact differential, an integrating divisor can be found, which is the same for all substances, and, depending only on the temperature, can be taken as the absolute measure of the temperature. The function S, thus shown to exist, defined by the equation

$$(2) \qquad dS = \frac{dQ}{\theta},$$

is called the entropy, and the two laws are mathematically stated when we say that there exist an energy and an entropy function. In the definition of entropy, the transformation is supposed to be reversible, or one which is the limit approached as the conditions of equilibrium are more nearly fulfilled. In an actual transformation, less heat is transformed into work than in a reversible one, or as, for the same heat taken in, more is thrown out without being utilized, the algebraic sum of all taken in dQ is less than if the transformation were made reversibly, accordingly

$$(3) \qquad dQ < \theta\, dS.$$

This second law of thermodynamics has been misused, especially by chemists and engineers, to prove that an infinitesimal amount of heat energy can *always* be decomposed into the product of two factors, one finite, which is here taken to be the temperature, and the other a perfect differential, as in many cases is actually true. The analogy with these cases is then supposed to demonstrate the existence of the entropy function, and to take the place of the mathematical and physical reasoning which justifies its employ. The fallacy of this reasoning appears when it is stated that in all practical transformations it is not the equality, but the inequality, that is employed.

Combining the equations of the two laws, we obtain

$$\theta dS \geqq dU + dW \tag{4}$$

and as soon as the work has been expressed in terms of the variables defining the state, the equation may be integrated. It may seem somewhat astonishing to the outsider that all of Gibbs's remarkable work with its extremely important consequences, many of which have been verified by experiment, while much more still awaits the experimental work which shall verify it, results from the careful consideration of this single total differential equation. Beginning with the simplest case, that of a homogeneous substance under no stress but that of a uniform pressure, the work done is given simply by the equation $dW = pdv$, so that our equation becomes

$$\theta dS \geqq dU + pdv. \tag{5}$$

At the same time we find that two variables, say the temperature θ and pressure p, completely determine the state of the body, so that the volume is given as a function of them. It then appears that, writing

$$dU = \theta\, dS - pdv, \tag{6}$$

the temperature and pressure are the partial derivaties of the energy by the entropy and the volume, taken positively and negatively, respectively. From this it follows that if we represent the properties of the substance by a surface whose vertical coördinate, for instance, represents the energy, while the two horizontal ones are the entropy and volume, the temperature and pressure at any state are determined by the inclination of the tangent plane, at the corresponding point, the inclination of whose intersections with two vertical planes parallel to the coördinate planes is given by the derivatives $\partial U/\partial S$, $\partial U/\partial v$. Thus from a knowledge of the energy as a function of the entropy and the volume, we obtain all the quantities with which we have to do, which is not the case if the temperature and pressure are taken for independent variables, because then we have to integrate the differential equation (5) in order to find U and S. But not only this. By means of the sign of inequality in (5) Gibbs is able to determine conditions for the stability of the existence of a substance in a particular state, and to give it a geometrical form, which states that if a particular state is one of stable equilibrium, the representative surface at the point in question will have both its principle curvatures of the same sign, or the surface will be convexo-convex downwards, if the energy axis is drawn upwards. Maxwell was so impressed with the importance of Gibbs's researches in this line that he constructed with his own hands a model of such a surface for water in its three forms, the original of which may still be seen in the Cavendish laboratory in Cambridge, and a cast of which he sent to Professor Gibbs, who had it in his lecture-room. Before the time of Gibbs, almost the only questions of equilibrium which had been systematically dealt with had been those which treated of the equilibrium of the same substance in two states of aggregation, such as water and ice or vapor. By means of an extension of the manner of regarding the question, Gibbs was able to lay down the laws of equilibrium of substances in any number of what he called *phases*; that is, different portions each by itself homogeneous, but different one from another not only physically but even chemically. Thus the foundation was laid for a general treatment of chemical phenomena. As soon as reversible processes could be devised for the removal from a particular phase, say a salt solution, of a particular constituent, say the water, for instance by evaporation, or by freezing out, it was possible to extend the differential equation to cover the equilibrium in question. If $m_1 \cdots m_n$ denote the quantities of different chemical substances contained in a given homogeneous *phase*, the equation is written

$$dU = \theta dS - pdv + \mu_1 dm_1 + \cdots + \mu_n dm_n, \tag{7}$$

and the quantities μ_r are called by Gibbs the *potentials* relatively to this phase of the various constituents. They thus afford a direct measure of the hitherto mysterious chemical affinity, and are the rates of increase of energy of the substance when unit quantity of the various substances is introduced without changing the entropy or volume of the phase. Thus to the conditions of dynamic equilibrium, that of a number of phases in presence of each other the pressure in each must be equal or there will be motion, and for thermal equilibrium that the temperature in each must be equal or there will be flow of heat, Gibbs adds the condition for chemical equilibrium, that for any constituent the chemical potential must be equal in every phase or there will be chemical reaction. As a consequence of this condition by the mere consideration of the number of variables involved, follows the celebrated *phase-rule*, which states that in any equilibrium the number of phases present cannot be greater than two more than the number of constituents. For instance, a single constituent, like water, can be present in three phases,— solid, liquid, and vapor, — but then with no freedom, that is, only at one determined temperature and pressure, the triple point of James Thomson. If on the other hand there are only two phases, say liquid and vapor, we have one variable in terms of which the others are determined, say the temperature, which completely determines the pressure of the vapor. This phase-rule has become of extreme importance and received great experimental development at the hands of the physical chemists. Of the other subjects treated in the papers, including a complete theory of capillarity and a development of the ideas of osmotic pressure and of dilute solutions, I have not time to speak. These researches were of such an abstract character, and were expressed in such severely logical form, almost devoid of particular examples, that for years they were very little known, and being published in a journal which was little accessible, they suffered still farther, until by the efforts of the chemists Ostwald and Le Chatelier, they were made at least partially accessible in German and French translations. May I not express the hope that Yale University will now see its way to give the scientific world an edition of the complete works of Gibbs in order that we may not be longer compelled to obtain a knowledge of them through the medium of foreign languages.

It is a pleasure to know that, in spite of the unfortunate circumstances noted, the value of Gibbs's thermodynamical writings was sufficiently appreciated during his lifetime to bring him the honor of the Rumford medal of the American Academy of Arts and Sciences in 1881, and the highest distinction of the Royal Society in its Copley medal in 1901.

The bicentennial of Yale University was signalized by the publication by Professor Gibbs of a treatise in its way quite as striking as his thermodynamical researches; namely, his Elementary Principles in Statistical Mechanics. We here have a generalization of these processes which when applied to the kinetic theory of gases had been attended with such fruitful results in the hands of Maxwell and Boltzmann. Gibbs here considered the conditions of so-called statistical equilibrium of a very great number of precisely similar dynamical systems; that is, systems determined by the same number of independent variables, with the same functions giving the kinetic and potential energies in terms of the velocities and coördinates, but with the states of the different systems, as determined by the values of the coördinates and velocities at any particular instant, varying from one system to another, so as to embrace all conceivable states. The question that then presents itself is: In what manner must these states be distributed, that is, how many of each must there be, in order that as the systems move in accordance with the dynamical laws that govern them all, the number of systems that are in any particular state shall not vary as the time goes on. Having found this condition, the next question is to decide upon the condition when the various systems are brought into relation so as to influence each other in some particular manner. To take the particularly simple example which led Maxwell to deal with the subject, consider a great number of very small material particles flying about in a given region at random; that is, with all possible velocities, and in all possible places. Supposing that all directions of the velocities are represented and that the number of particles whose velocities lie between u and $u + du$ is $\varphi(u)du$, then what must be the nature of the function φ in order that, when influencing each other by collision, or by the exercise of repulsive forces between pairs of particles, the value of φ shall be independent of the time. Maxwell found that the result was that $\varphi(u) = Au^2e^{-c^2u^2}$, or in other words that the rectangular components u_x, u_y, u_z of the velocity are distributed according to the law of probability, $e^{-c^2u_x^2}$. If there are a number of particles in statistical equilibrium it turns out that the mean kinetic energy for those of one sort is the same as for those of another sort, and this result leads us to what is known as Avogadro's law, one of the most important laws of physics for the chemist. If instead of a set of particles, each of which has three coördinates, we have a system depending on a greater number, such as a rigid body, with six, the theorem known by the name of Maxwell and Boltzman tells us that statistical equilibrium is attained when the kinetic energy is equally shared among all the different degrees of freedom for each coördinate system. For instance, if we consider a pair of material points bound together by a thin rod, forming a dumbbell-like model of a diatomic molecule, and characterized by five degrees of freedom, the mean kinetic energy of translation for all the molecules is three fifths of the whole energy, thus giving us the ratio of the specific heats equal to 1.4. These are practical conclusions of the kinetic theory of gases, and it is to the elaborate generalization of such theorems that Gibbs's work leads. The subject belongs to the mathematical theory of probability, with all the pitfalls which belong to that subject. A certain function of the state of the systems is found which, when they act upon each other, always tends to increase, and this is analogous to the thermodynamic entropy. It is in this manner that the deduction of the second law of thermodynamics, which has so long been sought as a consequence of the laws of dynamics alone, has its most promising mode of attack. Apparently this law is not to be deduced from the properties of a single system, but by averaging those of a great many systems similar to each other. It is not to be denied that if Gibbs has not succeeded in this deduction, which he modestly disclaims, he has at any rate made a great stride in the direction of success.

I can here only mention Gibbs's work on the electromagnetic theory of light, in which the same method of averages is used, and in which he makes noteworthy contributions to the difficult theory of dispersion. Finally, a few words on the subject to which Gibbs seemed to attach great importance, but which in my opinion is of far less importance than the work already mentioned. His attention was early drawn to the convenience for the physicist of the use of the notion of vectors introduced by Hamilton and Grassmann. Being dissatisfied with their notation, he devoted much attention to improving it, and made great use of it in his lectures. The great convenience of a system of vector analysis is now recognized by everyone, but how much of the short-hand advocated by one or another of its advocates is indispensible is still a matter for discussion. In my own humble opinion, what is necessary is the idea of a vector, and of the scalar or geometric, and vector products, along with that of the linear vector function and the notions of divergence and curl, while it is a matter of individual preference whether one shall write down the cartesian equations, or one of the three, or adopt a system of notation which may or may not convey more meaning to the eye, according to one's habits of mind. At any rate it may be said that, if present signs are to be trusted, there is as great a tendency to adopt the notation of Gibbs, as so well indicated and expounded in the treatise by his pupil, Dr. Wilson, as that of any of his competitors. With regard to the theory of vector analysis, considered as a branch of multiple algebra, to which Gibbs also made important contributions, I have no doubt that the pure mathematician will appreciate its value without need of the recommendation of the physicist.

I have spoken thus at length of the work of Gibbs, not only because his work was so good an illustration of my main thesis, but also because I believe that it shows him to have been possessed of one of the most commanding intellects that this country has produced, giving him the right to be ranked with Maxwell and the great names of the century now gone.

I pass now to some of the gains which physics has made in the last four years. The subject of radioactivity, which was then beginning to attract the attention of physicists, has since become of absorbing interest, and the extraordinary behavior of the element radium in the emission of energy without apparent source of supply has led us to expect developments of the greatest importance in our theoretical notions. Even the non-scientific public, ever avid of the sensational, has interested itself in the properties of radium to an extent only rivalled by the discovery of the Röntgen rays, and has apparently got the idea that radium is to undo the chief conquests in physics of the past. Of this, however, we have no fear, but we welcome the new discoveries, with the confidence that their mysteries will eventually be unravelled and will fit themselves into our system of mechanics without rupturing it. It is a pleasure to recall that in the subject of radioactivity one of the leading contributors has been, if not an American, at any rate a professor in an institution on the American continent, a member of this society and of its council, and a frequent contributor to its meetings, Professor Rutherford, of Montreal.

During the last year of the life of Rowland, one of his earliest and most important discoveries was called in question; namely, the magnetic field produced by an electric charge in motion. It would have seemed to require a daring and experienced experimenter to question the existence of a phenomenon which had been twice verified by Rowland himself, but such was the insistence upon the claim that it could not be ignored. It is a satisfaction to know that experiments carried on under the direction of Rowland during the last months of his life had again confirmed his conclusion, and that he died in the full conviction that he had made no mistake. Others took up the subject, with equally positive results, but still the suspicion would not down. Finally, by the combination of efforts of Mr. Pender, who had verified Rowland's results in Baltimore, and of M. Crémieu, who had apparently disproved them, working together in Paris, the ghost was finally laid, let us hope not to rise again.

Within the last two years another matter of great theoretical importance has been experimentally confirmed. Maxwell, in his treatment of light as consisting of electromagnetic waves, had shown that a perfectly reflecting body exposed to light incident normally should experience a pressure numerically equal to the density of energy in the medium in front of it. When Sir Wm. Crookes discovered the action of the radiometer thirty years ago, he at first supposed that it was the pressure of light which caused the action, until it was shown that the effect was of quite a different nature, being due to the action of the residual gases on the radiometer vane. This effect of Crookes had then to be eliminated before the pressure due to the light radiation itself could be observed, and this was at last accomplished, first by the distinguished Russian physicist, Lebedew, and then, but with far greater accuracy, by our colleagues, Nichols and Hull. This brilliant confirmation of Maxwell's theoretical conclusion, involving experimentation of the highest order, constitutes in my opinion one of those achievements of which American physicists should be most proud.

The subject of mechanical flight, whether it belongs to physics or engineering, is at any rate a good example of the truth that to any engineering invention there are three stages: first, the physical, in which the laws governing the process are determined; second, the engineering, in which it is found how they must be practically applied; and finally, the commercial, when it is found possible to put the invention into practice with profit. It is the two last stages that are most appreciated by the general public, which generally knows but little of the first. Thus the prolonged and well-planned endeavors of Langley to bring the question of flight successfully into the engineering stage, though very nearly crowned with success, have failed of popular acclaim, have been greeted with derision by a large part of the press, and made the author a target of abuse for congressmen, ignorant of the difficulty of the problem, and of the very great amount of meritorious work previously done by Professor Langley on the physical part, namely, the investigation of the laws of resistance of the air to the motion of plane surfaces. May we not, while according our admiration to these researches, also express the hope that the more practical investigations may also be brought to a successful conclusion. Pursuing the same object in a somewhat different manner, the brothers O. and W. Wright have met with even more success, and treating the problem of flight as it probably must be considered, namely as a species of athletic sport involving great skill in equilibration, and following on the lines of the unfortunate Lilienthal and later of Chanute, and learning the manipulation of soaring apparatus, have finally added mechanical propulsion, and made a successful flight of more than half a mile.

In his address, Professor Rowland lamented the lack of great endowed laboratories of research, and contrasted the amount of money devoted to the promotion of research with that devoted to armies and navies for purposes of destruction. In this connection we have some progress to report. To be sure, the United States is expecting to spend some ninety-six millions of dollars on the navy during the coming year, although not engaged in war, but the government has also established the Bureau of Standards, for the buildings and equipment of which $550,000 has been already appropriated, with a large annual appropriation including for the current year the sum of $85,000 for salaries. Under the broad policy of its director, Professor Stratton, this institution will be to a large extent a research laboratory, and plans have been made for buildings of such convenience, with so complete an equipment, that I feel confident that this laboratory will be little, if any, behind the German Physikalisch-technische Reichsanstalt, a comparison as flattering as any I know how to make. Those who saw last year at Washington what had already been begun, and the plans of the buildings now under construction, and who heard this year at St. Louis the account of the work by Professor Rosa, will, I think, agree that I have not overestimated the importance of this institution. Its work will not only influence the work of physicists in general, but will have the most advantageous influence on the work of instrument-makers in this country, and will tend to make us independent of foreign countries to an extent which has never been the case before.

Finally, as a further step in palliation of Rowland's reproach, we have the foundation of the Carnegie Institution, which to be sure has not the income of $100,000,000 per year desired by Rowland, but which is nevertheless a most generous addition to the material facilities in aid of scientific research, and which will, if wisely administered, undoubtedly have a most helpful effect in advancing the interests of science. To be sure, we find that last year the grants in physics were only five thousand dollars, while a single chemist obtained one half this sum, and for this year economic science has received a grant of thirty thousand dollars for a single object. Whether, as has been intimated to me, the representatives of physics were not sufficiently active in presenting plans of research, or whether the administrators of the Carnegie Institution had six times as much confidence in the representatives of economics as in those of physics, the result is equally unflattering to us, and we must strive to remove its cause. As I have stated above, I believe that the sending of Dr. Pender to Paris by the Carnegie Institution to investigate with M. Crémieu the Rowland effect, will, if it shall have permanently settled the existence of this effect, be of enough importance to justify the expedition of the whole sum appropriated to physics.

This is not the place for me to examine the record of this country as to its contributions to physics at large. I believe it will be generally admitted that in physics, as in other sciences, as in art and literature, our contribution has been painfully small, as compared with what might have been expected from a people as numerous, as energetic, and as prosperous as ours. The names of Franklin, Rumford, Henry, and Mayer, were the only ones mentioned by Rowland as constituting the "meager list of those whom death allows me to speak of and who have earned mention here by doing something for the progress of our science." To these is now to be added his own name, while among those still living are several whose work has won the admiration of the world. We have at any rate now the spirit, and many praiseworthy researches are here produced each year. If it is true that few capital discoveries in physics have originated in this country, to what is it due? Many replies suggest themselves. The application of so much energy to the subduing of a new country, the greater inducements offered by commercial success, the recent great material prosperity of the country, with a corresponding loss of ideality. It is undoubtedly true that the volume density of ideas connected with physics is as yet abnormally small in the atmosphere in this country, on account of the newness of the habit of inquiring of nature at first hand, and on account of the isolation of physicists from each other and from the European schools in which the habit of pondering on such subjects is old and well established. But I venture to propose another reason for this deficiency, not a sufficient reason, but to my mind an important one, and that is the insufficient equipment which American physicists have generally possessed in mathematics.

That this lack has been a real one hardly needs argument. Before the Civil War and even later, it was impossible to obtain instruction even in pure mathematics in anything worthy the name. The early years of the nineteenth century were great years in physical discovery, but the work of Fourier, Poisson and Cauchy, of Gauss, Green, Young, McCullagh, and Fresnel, remained a closed book in our universities. Those few rare searchers who took up investigation in physics were obliged to do so without the help that theory, embodied in mathematical symbolism, can give. But here it may be asked, in fact university presidents do ask, "Can one not become an investigator in physics without mathematics?" and the name of Faraday will be adduced as a convincing example to the contrary. To that may be replied that what was to Faraday practically a *tabula rasa* is now so thickly written over that the difficulty of making new discoveries is greatly enhanced, and the need of all possible equipment greatly emphasized; but also that in Faraday the lack of mathematical knowledge was compensated for by a most wonderful intuition, which in itself would have constituted him a genius. But even Faraday, with all his intuition, failed to show how electrical actions could be transmitted through the medium which he felt sure did transmit them, and the electromagnetic theory of light was left for another to invent. Maxwell, on the contrary, with his thorough mathematical equipment, taking up with enthusiasm the ideas of Faraday, was able to elaborate a system in which all the phenomena already known found a place, with room for the many not then known, which have since been found to justify his theory.

This example of Faraday and Maxwell may be made an excellent text for a discussion as to the object of experimental investigation in general. What is the use in observing the pressure of light? Is it merely that it is an interesting phenomenon, or is it because it fits into a great systematic arrangement of our knowledge of the mechanism of radiation, of the properties of energy and the laws of mechanics, as embodied in the differential equations representing the properties of the ether. Is there, I ask, a grander achievement of the human intellect than this same theory of the ether, not built up like the theories of the ancients on *a priori* grounds and hypotheses, but arrived at by a gradual process of logical reasoning as more and more experimental facts became known, and gradually taking on a simplified and comprehensible form, so that in the words of Lord Kelvin, ether is the only thing we know anything about. Why are we so interested in the confirmation of Rowland's observation that an electrified disk in rotation produces a magnetic field? Would that fact of itself be so important if it did not fit in with Maxwell's theory that charges are found at regions of divergence of the electric polarization of the medium, and that where this electric polarization is changing with the time, there is produced a magnetic field. Thus the phenomenon of Rowland takes its place as furnishing a term in the equations of Maxwell, explicitly introduced into them by Hertz, and contributing toward their symmetry and consistency. And if the Rowland effect does not exist, what becomes of the Zeeman effect, and of the determination of the mass of electrons by the curvature of cathode rays in a magnetic field?

But, it may be objected, the content of a theory, such as the theory of the ether, may be expressed in physical language without the employment of mathematical symbols and differential equations. Faraday's lines of force and his electrotonic state of the medium, it may be said, express as much as the triple integrals and the time derivatives of the mathematician. To a certain extent this may be true, but this extent must be very limited, and although, for instance, Faraday was able to state the law of induction of currents quantitatively in terms of the number of lines of force threading a circuit, without reference to a surface integral expressing the flux, he was not able to state the quantitative laws of distribution of energy in the medium, to describe the method of propagation of the energy in waves, or to foresee the mechanical pressure of the radiation.

Besides the argument resulting from the desire to coördinate our facts in a systematic theory, let us consider the practical help which mathematics affords to the experimental investigator as to what to look for. In the address from which I have so often quoted, Professor Rowland makes use of the statement that "a mathematical investigation always obeys the law of the conservation of knowledge: we never get out more from it than we put in." This when taken literally is to be sure true, but it would be a great mistake to infer therefrom the practical fruitlessness of mathematical investigation of natural phenomena. Consider the possibilities of transformation. Let us not forget that although chemical action obeys the laws of conservation of energy, still from the mixture of the sour nitric acid and the sweet and harmless glycerine we get the powerful nitro-glycerine, fraught with powers for good or evil. So in the hands of Maxwell the volume integrals of Gauss and Laplace representing action at a distance are transformed into differential equations representing action of the medium and propagation in time. This result is then left for experimentation to confirm, as it did in such a satisfactory manner at the hands of Hertz. As a further example, let us consider the position of an investigator of the conduction of heat who should be ignorant of the work of Fourier. To be sure, he might find out the laws of the stationary state, and this knowledge might stand to what we now have of conduction in the relation of the knowledge of steady electric currents to that of all the phenomena of variable and periodic currents of electricity. The laws of heat conduction are in themselves extremely simple, and are embodied in the law of Fourier that the quantity of heat flowing across an isothermal surface in a given small interval of time is proportional to the duration of the time, to the area of the surface, and, most important, to the rate of fall of temperature in the direction of the normal to the isothermal surface. This law of conduction together with the previously known one that the elevation of temperature produced in a substance by the communication of a quantity of heat is proportional to that quantity, leads to the equation for the propagation of heat by conduction,

$$\frac{\partial u}{\partial t} = a^2 \left\{ \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right\}.$$

In like manner our knowledge of the propagation of a sound wave consists in the two statements that the acceleration imparted to a small portion of the medium is proportional to the resultant of all the pressures acting on it, and that the component in any direction is proportional to the rate of decrease of pressure as we go in that direction, and secondly that the pressure produced at a point depends in a definite manner on the compression produced there, say according to the adiabatic law. These two statements again lead us to the differential equation for the propagation of sound, which is, what is not the least interesting, the same as that for the propagation of light and of electric waves, as the one just mentioned is also applicable to the diffusion of liquids or gases,

$$\frac{\partial^2 u}{\partial t^2} = a^2 \left\{ \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right\}.$$

Is there now, I may ask, anything in the nature of the physical laws involved or in the manner of stating them which would lead one to infer that there was any extraordinary difference in the two modes of propagation? Is there even any such marked difference in the differential equations? I think that you will agree with me that it would take a physicist of very great intuition to describe exactly what would occur in the two cases, if, for instance, a small region in an unlimited medium were to be the seat of an initial disturbance, in the one case representing a hot spot, in the other a region of compression, or electric or magnetic field. And yet the beautiful method invented by Fourier and developed by Cauchy leads to the integral of the conduction equation, in case the temperature is at a given time, $t = 0$, distributed in any prescribed manner $u = f(xyz)$, so that the temperature at any subsequent time t is represented by the integral

$$u=\frac{1}{a^3\pi^{\frac{3}{2}}}\int\int_{-\infty}^{\infty}\int f(\alpha\beta\gamma)e^{-r^2/4a^2t}\,t^{-\frac{3}{2}}\,d\alpha\, d\beta\, d\gamma,$$

where r represents the distance of the point $\alpha\beta\gamma$ from the point xyz. A glance at this integral tells the whole story, as follows:

The temperature of any point xyz is the additive resultant of the effects of all the initially heated points, each producing an effect dependent on its distance away, and on the time that has elapsed, in accordance with the factor $e^{-r^2/4a^2t}/t^{\frac{3}{2}}$ which, on discussion as a function of the time t and the distance r, gives the following results. The effect at the point xyz, no matter how far away, is *immediately* felt, the temperature rises to a certain maximum and then falls away, but the effect is never lost. The maximum temperature attained is less the greater the distance between the two points, and the rate of rise and fall is slower, but the striking thing is that some effect is immediately produced, as shown graphically by the curves which I show. Nor is the effect of the distance to be overlooked, for although the time of maximum temperature is greater the greater the distance, it is not proportional to the distance, but to its square. Thus we see how futile it would be to seek a velocity of propagation of heat, for there is none. This solution, when applied by Lord Kelvin to the propagation of electric current in a cable in which the effect of self-induction was neglected, showing that the maximum of signals would be received at times proportional to the squares of the distances, gave rise to the famous KR-law; and it was upon this basis that Lord Kelvin predicted the success of the Atlantic cable, by comparisons with the working of a short Mediterranean cable already existing. Here, then, was a practical result of a mathematical nature readily appreciated by capitalists of the caliber of Cyrus W. Field.

Contrast the result just described with the result of the same method applied to the second equation. Without writing down the result, or the transformation which enables us to interpret it, which is longer, we find that the effect at any point is the resultant of the conditions at other points, but that in this case the effect is not immediately felt, but that it comes on at a time directly proportional to the distance between the two points, passes over, and the effect is gone. Thus sound, light and electrical disturbances are propagated with a definite velocity in waves, and we are able at all instants to identify the separate effects of each point, or, as we may say, to interpret signals sent us without confusion with each other. It was by the discussion of the two terms in the integral of this equation that Kirchoff put the principle of Huyghens, and the explanation of interference and diffraction, upon a satisfactory dynamical basis.

In connection with the two differential equations which I have mentioned there comes the one which is an extension of them, and which arises when we attempt to find the law of propagation of sound in a viscous medium, of electric waves in a conducting dielectric, or of a telegraph line whose self-induction is not negligible. This gives the equation, first obtained by Kirchhoff,

$$\frac{\partial^2 u}{\partial t^2} + 2b\frac{\partial u}{\partial t} = a^2\left\{\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right\}$$

which has been called the telegraphist's equation, and which is of so much importance practically in connection with telephony and the transmission of energy by alternating currents. It may here be guessed with physical intuition that the physical nature of the propagation will combine the characters of both the other modes, and this the mathematical discussion will verify. Here the method of Fourier is again applicable, although this was long unperceived, and the labors of Heaviside, Picard, Poincaré, Boussinesq, and Brillouin have at last given us the general solution, which shows that while the propagation is by waves, and with a definite velocity, still the wave is in a measure wiped out as it proceeds, and leaves behind it a persistent trail which lasts indefinitely, and in telegraphy confuses the signals. The discussion of the solution, however, suggested to Vaschy and Heaviside what was to be done practically to improve the transmission, and render telephony possible over still greater distances. It was the results of a mathematical discussion of particular solutions of the telegraphist's equation, in a paper read in this room, that led Professor Pupin to the great improvement in telephony which he has so successfully completed. It is of the greatest importance that the method of Riemann, and the applications of it by Darboux, Picard and others, have enabled us to classify equations so that the matter of the propagation of discontinuities stands out in clear relief.

Let us now turn to the questions of the future or of the immediate present. What are they? Though the ether itself is now well understood, at least as to its mode of action, the nature of its connection with matter is now prominently under discussion, and the electro-dynamics of moving bodies is an extremely important subject for investigation. The importance of small charged bodies or electrons in the subject of radioactivity has aroused a very great interest in the question of the magnetic fields produced by moving charges, and every result of theory will be eagerly welcomed. Here the theory of Lorentz seems to be of the greatest promise, being an adaptation of Maxwell's theory to moving bodies, and the results of this theory have even led to the attempt on the part of Wien, Abraham, and others to explain dynamics itself on an electromagnetic basis, the inertia of a particle being due to the reaction of the magnetic field emitted by a moving electric charge (the Rowland effect). The question of the relative motion of the earth and the ether, with the explanation of aberration is occupying the attention of the most skilled talent, both experimentally and theoretically. The question of the mechanics of radiation, and the distribution of energy in the spectra of hot bodies is another subject of the highest importance, in which great progress has recently been made, and more is confidently expected. Besides these, there is the ever-present attempt to simplify matters by a reduction to dynamical explanations, particularly in the matter of thermodynamics, where the statistical methods of which I have spoken are undoubtedly to become of still greater importance. All of these subjects demand mathematical acumen and equipment of a high order, and it seems needless to argue the absolute necessity of such equipment to the successful physicist wishing to contribute in large degree to the extension of the world's knowledge. To the objection sometimes made, that the two kinds of mind, which are fitted at the same time for experimental discovery and for mathematical research, are rarely combined in the same person, and the suggesstion that the physicist ally himself with some mathematician who shall solve his theoretical difficulties, I reply that such happy marriages are rarer still, and that lacking an extraordinary amount of sympathy and insight on the part of the mathematician, the advice of Miles Standish is still good,

> "If you wish a thing to be well done,
> You must do it yourself, you must not leave it to others."

As examples to illustrate my point, I may mention the names of Helmholtz, Lord Rayleigh, and Hertz, of whom it would be difficult to say whether they excelled most in theory or experiment.

We come then to the practical question, how much and what portions of mathematics are necessary to the physicist, and how may the student be provided with them. It is unnecessary to say that first of all comes a thorough acquaintance with the infinitesimal calculus, with the ability to make use of it in manifold applications. Of these, the most important is mechanics, the foundation stone of physics, and the portion which we wish to include everything else. Upon a thorough training in mechanics one cannot too strongly insist. And here it will not suffice to be content with the elementary notions, but the student must understand and be practised in the meaning and use of Lagrange's equations, and be acquainted with the methods used in the treatment of continuous media, as well as of discrete points. The subject of differential equations is of fundamental importance in all physical applications, and that of linear partial differential equations with constant coefficients should receive particular attention. As an indication of what is desirable in this direction I may mention Byerly's treatise on Fourier's series and Weber's reconstituted lectures of Riemann, of which the first may be especially commended for the many examples for practice furnished the student, and the latter for the greater variety of methods with which it gives acquaintance. The subject of the theory of functions of a complex variable is of such manifold importance in its physical applications, especially in connection with the conformal representation of surfaces, and with the linear differential equations with variable coefficients that arise from physical problems, that it must not be neglected. I believe also that it is impossible for the physicist to be too familiar with geometry, and in particular with those applications of the calculus usually denoted by the name differential geometry, as applied to the study of curves and surfaces.

Having arrived at this point, I take the liberty of addressing myself to the mathematicians, and contemplating briefly the other side of the shield, by showing what they are to gain from the alliance with the physicists. I need hardly recapitulate the debt which mathematics owes to physical questions for proposing fruitful fields of inquiry. There is no need to go back to ancient times to speak of the measurement of land as giving the impetus to the study of geometry, or even to the time of Newton, whose attention was chiefly occupied by physical questions. From the time of Laplace and Lagrange, the greatest mathematical intellects have concerned themselves with physical matters. Gauss, who by common consent is without a peer in his century, was the author not only of the "Disquisitiones Arithmeticæ" but also of the "Forces acting according to the inverse square." To how many investigations in the theory of differential equations and the theory of functions has the equation of Laplace given rise! Was not the investigation of Dirichlet on the convergence of trigonometric series, brought to the attention of the world by their application by Fourier to physical problems, the beginning of the modern critical study of functions of a real variable, and has not the subject thus begun been one of the most prolific in all modern analysis? Did not the differential equations which have been most thoroughly studied, namely the linear differential equations of the second order, originate from the method of orthogonal curvilinear coördinates, applied by Lamé to the study of the partial differential equations of physics? Was not the subject of the Calculus of Variations called into existence, and does it not still draw most of its problems or examples from physical questions? I will mention only brachistochrones and minimal surfaces. Even such exponents of the "purest" or least applied species of mathematics as Weierstrass and Kronecker found an application of the theory of elementary divisors in Lagrange's problem of small oscillations, while the attention paid to physical applications by Poincaré, Picard and Klein is well known. But there is a still more practical reason that the mathematician should concern himself with physics, to a degree that is by no means uncommon in Europe, but is I believe far from common in this country. I may say in fact, to speak in language that is sure to be understood in America, that it will be money in the pocket of the mathematician to make himself acquainted to a large extent with physics, and with the needs of physicists and even of engineers. Many a promising student, who has earned his doctor's degree in pure mathematics finds himself obliged to teach applications to physics, and what is likely to be his state of mind, however familiar he may be with the theory of groups or with the properties of power series, if he knows nothing of the potential function, of dynamics, or of spherical harmonics? I have even known mathematical graduates to have to teach thermodynamics and the strength of materials, and in engineering schools this is by no means infrequently the case.

I hope then that I have said enough to show that the interests of mathematicians and physicists are to a large degree identical, and that each can well profit by the work of the other. At any rate, they are both equally interested that the instruction in mathematics in the schools should be improved, and that throughout school and college the most practical methods should be adopted, with the minimum of waste. In this matter I am thoroughly in accord with the ideas expressed by Professor Moore in his presidential address to the American Mathematical Society a year ago, particularly in what he says with regard to the unification of pure and applied mathematics. The complaint is often made of the instruction in the schools that the algebra, and even the geometry, is largely meaningless to the scholar because he does not have any use for it. Now mathematics, though it has undoubtedly its *raison d'être* if regarded simply as an intellectual achievement, is for the great majority of those who use it a tool, to be mastered because one can do something with it, and the sooner that the student learns what he can do with it the better. I believe then that with every step in advance in algebra or geometry should be connected some application, so that the drawing-board, the slide-rule and the performance of experiments in physics should all be closely bound together. In fact I would go so far as to wish that all the school mathematics and physics might be taught by the same person, or if this is not possible, that the work of the two departments should be in the hands of teachers in the highest sympathy with each other's work. In this regard I share the desires of Professor John Perry in England, who is continually contending for the extension of the teaching of the useful and interesting rather than that of the formal or strictly logical.

I shall now attempt briefly to sketch out a course, such as I think a student of physics should have, and to show that it is quite practical, and that without making inordinate demands. I claim no originality, as such courses are in existence at many of our leading institutions — I wish merely to urge that all intending physicists take them. I will suppose that the school course in geometry, algebra and physics has been organized as described by Professor Moore, and that the boy comes to college familiar with the elements of algebra, including the complex diagram, skilled with the drawing-board, the ruler and compasses, and practised in numerical computations, the use of tables and squared paper. He should also know enough of plane trigonometry to get along with — it is astonishing how little that is.

Most of our colleges now have four year courses, and a students spends in addition three in graduate work before taking his degree. It will not be long before the college course is reduced to three years, whether we approve or no, and while it is not possible to make a physicist or mathematician in six years, we can at least give him a good start, and launch him on the scientific sea prepared to navigate for himself, without expecting him to make shipwreck. During the first year he will naturally devote himself to analytic geometry, of two and three dimensions, for I believe that soon after beginning they may be studied together, and to learning enough of the elements of the theory of equations and of determinants to apply them in geometry. By the end of this year he should have been introduced to the elements of calculus, without which I do not believe it pays to study analytic geometry. In connection with the analytic geometry he may also learn the elements of vector analysis, which is largely a matter of notions and notations. If anyone doubt the possibility of doing this in a year's course of five hours a week, I recommend him to read the preface of Perry's calculus, and see what that gifted teacher has himself accomplished. During the second year he should attack the calculus in a serious manner, guided by a text-book covering the subject matter of, say, Lamb's admirable text-book, learning at the same time more analytic geometry, and supplementing the examples with many from different parts of physics, such as are bountifully supplied by Perry. During this year he will certainly have made the acquaintance of mechanics, in a more satisfactory way than was possible the year before, and by the end of the year will have a good deal of practical knowledge of differential equations. Of course the squared paper and the drawing-board will have been in constant use. The third year he will get at partial derivatives with a multitude of examples, definite integrals, an extremely practical subject for the physicist, and differential geometry. To give a concrete idea of what I mean, I will suppose the subject matter to have been covered in these three years that is contained in Lamb's and Perry's Calculus, Appell's Elements de l'Analyse mathématique (an extremely attractive and practical book), and perhaps half of Scheffers' Anwendung der Differential- und Integralrechnung auf Geometrie. The student will then be prepared to take up mathematical physics in earnest, and during the next three years the systematic study of differential equations occurring in physics, with the developments in series of functions of Fourier, Bessel, Laplace and Lamé, the theory of functions and of infinite series and the mathematical theories of electricity and light, sound and heat, all preceded by a liberal amount of mechanics, including elasticity and hydrodynamics, will have no terrors for him. It may be asked whether I would require all these subjects for the doctor's degree. I reply that I certainly should, if by that degree is meant an adequate preparation for life, understanding by "life" in this case the contribution of original work to the world.

In the college work I believe that it would be of mutual advantage not to separate the two classes of students, mathematical and physical, nor them from those who pursue the subjects merely for their educational value, but in the university practical requirements may require a modification of this opinion. Here, again, I appeal to my mathematical colleagues that they have the greatest sympathy for the needs of physical and engineering students who may come under their teaching. Remember that though they, too, may have good brains and appreciate accurate logic, still to them mathematics is a thing to do something with, and that they require more than proofs that things are so, the knowledge that they may be used. Do not concentrate your attention upon existence theorems, or upon the question of the convergence of series to the exclusion of what I may call the probable conditions of convergence. On this point I may call attention to the views of Professor Klein in his last book, On the Application of the Calculus to Geometry, and to his remarks on approximation-mathematics. Of course, it is necessary to know what uniform convergence is, and that it is not always possible to differentiate or integrate a series term by term, but surely the instruction should lay more force on "thou shalt" than on "thou shalt not."

A friend of mine describes the effect on students of the teaching of one of his ablest colleagues, by saying that they are so scared that they never dare to integrate, differentiate, or touch an infinite series, for fear that something awful may happen. How different is this from the methods of Fourier, Green, Maxwell, and more recently of Heaviside, who, all untrammeled by academical restrictions, proceeds with the most extraordinary facility to make new contributions to our knowledge, leaving to other less original minds the task of demonstrating the correctness of his methods.

Let no one say that it is impossible to steer the difficult course between the Scylla of rigor and the Charybdis of inaccuracy, for it has been done by excellent professional mathematicians in a way to be both attractive and profitable to the physicist. I need only instance the admirable Analytisch-Funktiontheoretische Vorlesungen of Fricke (whose Differential Calculus I would also commend in the same breath as that of Perry, though a great contrast to it) and in the Partielle Differentialgleichungen of Weber, whose rewriting of Riemann's course has maintained the clearness and elegance it had, while adding immensely to it in variety. A course on these two books would constitute a liberal education in mathematics for the physical student, practical in the highest degree.

I have now sketched in a rough way what I think we can do for the aspiring physicist in the way of providing him with a mathematical panoply, and that without preventing him from spending the proper amount of time in the laboratory and of devoting a reasonable amount of time to the study of English, French or German, or even Latin and Greek. Fifteen hours per week is not too much to spend in the classroom while in college, and I believe that if the physical or mathematical student divides this equally between physics, mathematics and general culture, he will be safe. To those who demand that all the time in college should be devoted to general culture and none to preparation for the business of life, I have only to say that they do not understand the exigencies of the strenuous life of scientific research. I regret, as much as they do, that there should be any physicists ignorant of Greek, to say nothing of Latin. What little of them I know I would not exchange for any number of definite integrals, or even milligrams of radium. Culture and the love of the beautiful and of the ideal we must all have — the more the better; but let it be understood that this may come in different ways, and that we cannot all read the same books or think the same thoughts. Let not the poet, the musician and the painter set themselves over against us, however, and rail at us as devoted to the material. If they do so, they do it in ignorance, and let us not antagonize them, for we strive for the same ends. Ours is as idealistic a pursuit as that of the poet, and calls for as much imagination. It is an intellectual joy that we strive after, which nature affords to us as well. Is the sky less blue to us because we can specify its wave lengths, or because we know that its color is due to diffraction by small particles? Is the music less sweet because we can resolve its motion into harmonics and develop it in a series of normal functions? I think not. It seemed to me particularly appropriate to see a fine pipe-organ in the drawing room of a great physicist, equally noted for his mathematical and experimental contributions. Far be it from me to wish to substitute for Southey's description of "How the Water Comes Down at Lodore" —

"Thumping and plumping and bumping and jumping,
And dashing, and flashing, and splashing and clashing,
And so never ending, but always descending,
Sounds and motions for ever and ever are blending,
All and at once and all o'er, with a mighty uproar —
And this way the water comes down at Lodore," —

the statement that it descends with a uniform acceleration of 980 centimeters per second per second, modified by the effect of viscosity and impact, and subject to the equation of continuity, that the vapor tension about drops of spray is larger than over smooth water, and that the region about is abnormally defective in radioactivity. Both sorts of statement have their place, and both appeal to the imagination. There are times when fact is of the most consequence; other times when fancy. The lines of Tennyson,

> "Every moment dies a man,
> Every moment one is born,"

are surely not improved by Babbage's suggested emendation in the interest of accuracy,

> "Every moment dies a man,
> And one and a sixteenth is born."

But facts lead to fancies, and in the quest of nature's secrets, we are lifted above the material philistinism of every-day life.

May the Americal Physical Society, and the American Mathematical Society ever continue their ways, like twin sisters, hand in hand, in pursuit of the good, the true and the beautiful.

THE CONDUCTION OF ELECTRICITY IN MERCURY VAPOR.[1]

By A. P. Will.

If X represent the electromotive intensity in volts in the positive column of a tube containing saturated mercury vapor carrying a current of electricity, then

$$X = f(I, \Delta, D)$$

wherein I represents the current in amperes, Δ the vapor pressure in millimeters of mercury, D the diameter of the tube in centimeters. An approximate empirical form for the function f was determined; also the numerical values of the constants involved were found. This was accomplished by making experiments upon tubes of different diameters (varying from 1.25 cm. to 5.08 cm.) with different currents (varying from .5 of an ampere to 3 amperes) at different temperatures, care being taken that the measurements were made when the vapor was saturated. Thus the vapor pressure and the vapor density could be deduced. Two thermo-couples were introduced into a tube about midway of its length at a distance from each other of about 15 centimeters. These served at once as a means of determining the temperature and the drop in potential, the latter being measured by a Kelvin electrostatic voltmeter.

It was found that for a constant current and a constant diameter the relation between X and Δ is linear up to a certain pressure Δ_Q while for higher values of the pressure the relation though still linear is represented by a line of lesser slope. The pressure Δ_Q depends upon both the current and the diameter.

The approximate form found for f is

$$X = a\left\{b + \frac{1}{\sqrt{I}}\right\}\left\{c + \frac{1}{\sqrt{D}}\right\}\left\{\Delta + \frac{1}{\sqrt{D}} + \frac{2}{D}\right\} + \alpha,$$

wherein a, b, c, and α are constants which suddenly change in value when the pressure Δ_Q is reached; the numerical values of the constants which do not change appear in the equation. The numerical values of the constants which jump in value are:

	Below Δ_Q	Above Δ_Q
a	.055	.15
b	.775	.398
c	1.71	.122
α	.10	.37

---

[1] Abstract of a paper presented at the meeting of the Physical Society held on February 27, 1900.

It was difficult to determine Δ_Q as a function of the current and the diameter very accurately but a rough approximation is

$$\Delta_Q = K \frac{\sqrt[4]{I}}{\sqrt{D}},$$

wherein $K = 4$.

The main part of the discussion was with reference to the positive column. But the matter of the drop in potential over the anode and over the cathode was also touched upon. The potential drop over both anode and cathode depends but slightly upon the current. Over the anode the drop in potential is about 7 volts and over the cathode about 5 volts. Under abnormal conditions, for instance when the anode is covered with a bluish, velvety haze the potential-drop over it may rise to 15 volts or more.

The experiments were carried out in the laboratory of Dr. Peter Cooper Hewitt, without whose collaboration the work would have been impossible.

PRELIMINARY MEASUREMENT OF THE SHORT WAVE-LENGTHS DISCOVERED BY SCHUMANN.[1]

By Theodore Lyman.

FOR the past few years the author has been engaged in an attempt to measure the short wave-length discovered by Dr. Victor Schumann, but it is only recently that this attempt has proved successful.

Working in an atmosphere of hydrogen with a concave diffraction grating ruled upon speculum metal, an "end-on" tube filled with hydrogen gives numerous lines below the aluminum group at 1854.

The shortest wave-length so far observed has a value of 1178 Ångström units. The limit of error is two units.

It is interesting to note that, contrary to expectation, speculum metal is able to reflect these very short wave-lengths to a considerable degree.

This is but a preliminary notice. The author has in preparation a complete list of these new wave-lengths. He has also good hopes of still further extending the spectrum.

It is the author's purpose to publish a detailed account of the investigation in the Proceedings of the American Academy, and perhaps elsewhere.

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[1] Abstract of a paper presented at a meeting of the Physical Society held on February 27, 1904.

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BY
EDWARD L. NICHOLS
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XCVIII

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PHYSICAL REVIEW.

POTENTIAL PHENOMENA IN VACUUM TUBES DURING THE PRODUCTION AND INTERRUPTION OF ELECTRICAL DISCHARGE.

By S. N. Taylor.

WHEN electrical energy is passing between the electrodes of a vacuum tube we know that the discharge may be either direct or alternating, continuous or disruptive; but not very much seems to be known, except in the case of the continuous discharge, concerning the variations in potential which occur in any of these cases. It was with the hope that something more might be learned regarding this question that, at the suggestion of Professor E. Wiedemann, I began the investigations described in this paper. The work was done in the Physical Laboratory of Erlangen University and I have to thank Professor Wiedemann for many valuable suggestions made during the continued progress of the work. Professor Schmidt and Dr. Wehnelt also have given valuable assistance.

Numerous experiments have been made in connection with the work, but this paper attempts to give only some of the preliminary results obtained. More complete results will be given later when other tests have been completed.

General Outline of the Work.

The first series of tests were made by calorimetric methods. Judging from previous results obtained by other investigators, it was thought that, if the anode were connected to earth, the average fall of potential at the cathode for either continuous or disruptive discharge could be determined from the total heating effect, using the well-known equation $H = 0.24\ EI$. In the course of the experiments, however, it appeared that better results could be obtained by means of the Braun tube, and after making simultaneous determinations by the two mothods the heat measurements were for the time being discontinued.

By means of the Braun tube we were not only able to determine the potential difference with considerable accuracy, but also to observe the variations of potential and the frequency of discharge. By means of it new and interesting facts were found out regarding the maximum and mininum potential of disruptive discharge; namely, that the potential rises to a certain maximum height and then suddenly falls off to a minimum value, but never to zero. Both the maximum and minimum values for any tube depend upon the particular conditions under which the tube is tested.

In connection with the work, a method was found by which the Braun tube can be conveniently used to measure high potentials, say of 1,000 or 1,200 volts, where the fluctuations are not too great. When the limits of variation are great, however, say 500 volts or more, the problem becomes more difficult; but a new method is given below which overcomes those difficulties quite satisfactorily.

The measurements show that the manner in which the potential develops and falls off is very largely affected by the capacity of the circuit.

Tests were also made to ascertain the effect upon the potential produced by reversing the direction of the current or by interchanging the electrodes, which show why certain results obtained by other investigators are in disagreement with one another.

I. Apparatus.

The apparatus used in these tests included a storage battery of 1,120 cells, a twenty plate influence machine driven by a Schmidt water motor, a single plate influence machine driven by an electric motor, two Sprengle pumps, McLeod pressure gauge, a Wiedemann galvanometer, with rubber insulated coils, having a constant of 38×10^{-6} amperes per centimeter, two telescopes, a rotating mirror, sensitive thermometers, two Kohlrausch condensers, an electric tuning fork, two static voltmeters reading to 10,000 volts, a Kelvin multicellular voltmeter, a telephone receiver, and vacuum tubes of various forms. In addition to these the parts which call for special description are as follows:

(*a*) *Cup Calorimeter.* — Fig. 1 shows a simple form of calorimeter discharge tube. *A* denotes a vacuum tube about 22 mm. long and about 13 mm. in diameter, surrounded by a glass calorimeter vessel *B* into which a liquid is placed. Both parts are made as small and light as possible so that the changes in temperature produced by the passage of the electrical discharge through *A* will be as great as possible. The water equivalent of the whole apparatus including the thermometer and 6 cubic cm. of terpentine, was found to be 8.03 by careful measurement.

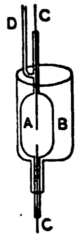


Fig. 1.

(*b*) *Apparatus D* as shown in Fig. 2 is a form of the Bunsen calorimeter as modified to meet the requirements of these investigations. It is all made of glass and all the joints are fused, except *WW* where the aluminium electrodes *GG* are sealed in with wax. The vacuum tube *A* is enclosed by an outer vessel *BC* of which the upper part *BB* is filled with benzol and the lower part *CC* is filled with mercury all air being carefully removed. *M* and *N* are ground glass stopcocks and *E* is a tube which is convenient for introducing the liquids into the outer vessel. When *BC* has been filled with benzol and mercury, *N* is closed and *M* is opened. Then when the electric discharges are developed in *A*, the benzol becoming warmed expands and causes the mercury to rise in the capillary tube *DD*. The bore of *DD* being less than a millimeter in diameter, a very slight change in the temperature of the benzol produces a large variation in the length of the mercury column. A millimeter scale being placed directly behind the mercury column, the length of the col-

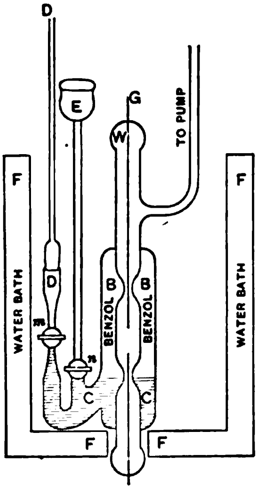


Fig. 2.

umn can be read to a tenth of a millimeter by means of a telescope placed some distance away.

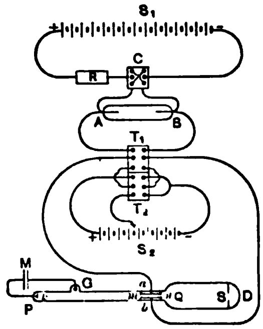


Fig. 3.

(*c*) The Braun tube as used in these measurements is the form adopted by Dr. A. Wehnelt (Verhandlungen der Deutschen Physikalischen Gesellschaft, January, 1903) for potential comparisons, the potential plates being inside the glass tube. The form is represented in Fig. 3 where *PQ* is a glass tube 53 cm. long and 3 cm. in diameter fused to a larger cylinder *QD* 22 cm. and 8 cm. in diameter. *S* is a fluorescent screen fastened to the walls of the large tube by means of glass plugs. The cathode *k* consists of an aluminium disc 1.5 cm. in diameter located at the extreme end of the small tube as far from *S* as possible. The anode *G* is situated in a short side tube which projects perpendicularly from *PQ* about 15 cm. from the end *P*.

The potential terminals *a* and *b* are flat plates of aluminium 8 cm. long and about 2 cm. wide. To the center of each of these is riveted a thick aluminium wire which, passing through the walls of the tube, is firmly attached to the glass. The plates are thus held rigidly in position 2 cm. apart and parallel to the axis of the tube. Electrical contact is made with them by means of platinum wires sealed in the glass. At each end of these plates is a mica diaphragm *m* and *n* fitted closely to the inner wall of the cylinder. The diaphragm *m* has an opening at its center only 1 mm. in diameter but the opening in the diaphragm *n* is some twenty millimeters in diameter. The purpose of these diaphragms is to intercept all unnecessary cathode rays. The bundle of rays which enters between the plates is only one millimeter in diameter, and that will be the size of the bright spot produced by it upon the fluorescent screen. Thus when a sufficiently high vacuum has been produced within the tube, and some 8,000 or 10,000 volts have been developed between the electrodes, a small greenish bright spot will be seen upon the screen *S* and its position thereon can be accurately read by a suitable scale. If, however, there is a difference of potential between the plates *a* and *b* the cathode ray will be deflected; the displacement of the spot upon the screen will be proportional to the potential difference, and affords a method of potential measurement.

(*d*) For measuring the displacement of the fluorescent spot upon the screen the method used was as follows: A telescope was placed in convenient position some 2 meters away from the Braun tube and focused upon the screen *S*. At the left of the telescope and at a distance from it equal to that between the telescope and the screen, was placed a millimeter scale made of thick plate glass upon which the divisions and numbers had been cut by means of a diamond. One end of the scale was fitted tightly into an opening made into an opaque box. Inside of the box was placed a lighted glow lamp, and the only light transmitted from the box was made to pass through the opening into which the scale was fitted. The light which was thus emitted passed through the entire length of the glass plate and being totally reflected internally by the polished walls of the glass, nothing of the scale could be seen in a dark room, except the division marks and numbers which stood out as so many bright lines. With proper adjustment this scale could be read very distinctly several meters away. By means of a mirror obliquely placed the image of this illuminated scale was reflected into the telescope in such a way that the spot on the screen *S* which could be seen at the same time through the telescope appeared to be located upon the illuminated scale. Thus the position of the fluorescent spot could be read at any time, and any change in its position or displacement of the spot could be thus read in millimeters.

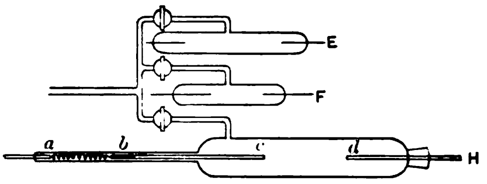


Fig. 4.

(*e*) *Discharge Tubes.* — To test the effect produced by having the discharge take place under different conditions various discharge tubes were used, some of which are represented in Fig. 4. The tubes *E, F* and *H* were connected to the vacuum pump at the same time so that the vacuum condition would be the same in all of them and the difference in the discharge phenomena obtained from them, if any, would be due simply to the different forms or dimensions of the tubes. The dimensions of these tubes are as follows:

Tube.	*E*	*F*	*H*
Diameter,	3 cm.	4 cm.	4.5 cm.
Length,	32	21	65
Distance between Electrodes,	1.5	14	Variable.

In tube *H* the electrodes are aluminium with the exception of the portion which connects *a* to *b* which is a fine copper wire wound in a spiral, while the portion *b* is iron and attached rigidly to *c*. If a strong electromagnet is applied to the outside of the tube the position of *bc* can be changed at pleasure and the distance between *c* and *d* can be made any desired magnitude.

II. Method of Determining the Mean Potential Difference by Calorimetric Methods.

If the total heat developed in the discharge tube can be measured then $H = 0.24EI$ and knowing the current I we can calculate the mean potential E. All heat measurements were made with the apparatus surrounded by a water jacket kept at constant temperature. In addition to this precaution, corrections were always made for radiation by observing the rate of gain or loss in temperature for the five minutes immediately before the current was turned on, and for the five minutes immediately after it was turned off. The current was always passed through the tube for ten minutes and a mean correction for the radiation was thus calculated.

The first heat measurements were made by the simple cup calorimeter of Fig. 1. In these the changes in temperature were measured directly by sensitive thermometers which were read accurately to tenths of a degree and estimated to hundredths of a degree by means of a telescope. The current which, passing through the tube, cause the rise in temperature, was measured by the Wiedemann galvanometer with rubber insulated coils, the constant of the instrument being 38×10^{-6} per centimeter deflection. The potential as derived from these measurements however, was very much less than expected and led us to look for a more sensitive method. Accordingly, to meet this requirement the calorimeter which we have called apparatus *D* was constructed as in Fig. 2 which proved to be very sensitive and gave better results. To obtain the best results the readings were taken in a room of nearly constant temperature and the apparatus was surrounded by a constant temperature water jacket, corrections for radiation being made here as in the previous case.

To calibrate the apparatus a continuous current of measured intensity and potential was discharged for a known length of time through the tube. Thus a known quantity of heat was developed within the tube and the rise of the mercury column produced by it was carefully measured. After correcting for radiation, it was found that a rise of one millimeter of the mercury column corresponded to 0.2049 calories of heat developed in the tube, or in other words the constant of apparatus *D* was 0.2049 calories per millimeter. A number of calibrations of this kind gave results which differed only very slightly in the third significant figure. Some of these measurements are given in Table I. together with the potential measurements taken simultaneously by means of the Braun tube. As in this case the heat in the tube was developed by a continuous discharge in one direction, only one potential difference would exist between the electrodes and therefore only one potential value is given by the Braun tube.

Table I.

Calibration of Apparatus D, by means of continuous discharge, together with simultaneous potential determinations made by means of the Braun Tube.

Test No.	Potential Determinations by Means of the Braun Tube.						Heat Determinations. Calibration of Apparatus D.				
	Position of Fluorescent Spot.				Potential Derived.		Potential by Kelvin Volt Met.	Current by Wiedemann Galvanometer.	Heat Devel. by Current in 10 Min.	Rise in Hg Col. Corr. for Radiation.	Calories per mm. of Hg Column.
	For Unknown Potentials.		For Known Std. Potentials.								
	Max. x	Min. y	$V=480$. a	$v=240$. b	Max. X	Min. Y	Volts	Amps.	Total Cal. Q	Total Rise. h	Q_0
1	5.1	5.1	6.1	4.6	320	320	317	.000509	23.22	11.34	2.047
2	5.3	5.3	6.2	4.8	326	326	325	.000777	36.37	17.70	2.055
3	5.9	5.9	7.0	5.3	325	325	325	.000771	36.101	17.65	2.045

Average $Q_0 = 2.049$

III. METHOD OF DETERMINING THE LIMITS OF POTENTIAL DIFFERENCE BY MEANS OF THE BRAUN TUBE.

At the same time that the heat method was being perfected, tests were also being made by means of the Braun tube which proved to be the better method for present purposes. The method was as follows:

Potential leads connected the electrodes *AB*, Fig. 3, of the discharge tubes to the potential plates *Ab* of the Braun tube, then whenever there was a difference of the potential between *A* and *B* the same potential difference existed at *ab*, and caused a displacement of the fluorescent spot upon the screen *S*. Moreover the displacement was proportional to the potential difference and when read off on the illuminated scale which has been described, it afforded a means of measuring the potential. The potential of a constant discharge between *A* and *B* is constant, and the round fluorescent spot accordingly remains steady upon the screen at whatever point the constant potential difference places it. The varying potentials of a disruptive discharge cause rapid oscillations of the spot, which produces a thin, bright, fluorescent line upon the screen varying in length according to the potential variations at *AB*. A constant potential of two or three hundred volts or more at *AB* may cause the spot to disappear. The reason for this is that the applied potential bends the cathode rays so much that they no longer fall upon the screen. The spot or line can be brought back again, however, in a very simple manner by means of the electromagnets placed opposite the plates. The magnets should be so located that their magnetic lines of force are perpendicular to the axis of the Braun tube and parallel to the plates. Increasing the strength of the magnetic field decreases the whole deflection of the cathode ray proportionally and thus brings the spot upon the screen. If the field thus produced is uniform and constant, the displacement of the spot will still be proportional to the potential difference between the plates, though the displacement will be less than before. The deflections produced by the potential differences, as thus affected by the magnetic field, can now be calibrated by direct comparison with known potentials in the following way. The connections given in Fig. 3 show the method of calibration used in these measurements. An upward throw of the transfer switch T_1 places the plates *ab* of the Braun tube in connection with the electrodes *AB* of the discharge tube. A downward throw places *ab* in connection with the terminals of storage battery S_2. While this is down, changing the position of the transfer switch T_2 places upon the plates *ab* either of any two standard voltages of battery S_2 which may be chosen for purposes of calibration. The best results were obtained when, for this purpose, standard voltages were selected which coincided as nearly as possible with the unknown limits to be measured. Moreover, the deflection should be calibrated for each observation at the instant that the observation is made, for the length and position of the fluorescent line varies instantly with any slight change in the vacuum conditions of the Braun tube. By means of the telescope, the limits of the fluorescent line or the position of the spot, was read upon the luminous scale, first with the Braun tube connected to the terminals *AB*, then to a known high voltage and immediately afterward to a known low voltage of battery S_2, these adjustments being rapidly made by the transfer switches T_1 and T_2. Having thus obtained the readings for the two known voltages we can calculate the unknown voltages corresponding to the other points read upon the screen at that time. The maximum and mininum voltages for any oscillation of the spot of course will be the points represented by the upper and lower ends of the fluorescent line. Thus if x and y are the readings upon the scale corresponding to the upper and lower ends of the fluorescent line, as produced by the various potentials to be measured, and if a and b denote the two points upon the scale corresponding to the two known calibration voltages, V and v, then the unknown voltages X and Y corresponding to the two readings x and y will be

$$X = (x - a)\left(\frac{V - v}{a - b}\right) + V$$

and

$$Y = (y - b)\left(\frac{V - v}{a - b}\right) + v.$$

This magnetic method of diminishing the fluorescent displacement does not apply for the measurements of potential variations which exceed the limits of the fluorescent screen. Thus for example, by means of this method I could measure the potential difference between 750 and 900 volts, but could not measure the difference between 300 and 900. For if the magnetic field were made strong enough to bring the deflection corresponding to 900 volts down upon the screen, then that corresponding to 300 volts would fall below it.

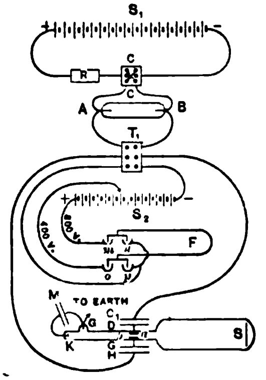


Fig. 5.

For the measurements of wide variations of potential of this kind the following method of diminishing the fluorescent displacement was employed successfully. Two equal condensers *CD* and *GH* having movable plates were placed in series with the potential plates *ab* of the Braun tube, as indicated in Fig. 5. Only a fraction of the total potential then fell upon the plates *ab* and by adjusting the distances between the plates of the condensers the fluorescent displacement could be made as small as desired. Since a constant potential applied to the condensor plates *C* and *H* only produced an instantaneous effect upon the fluorescent spot, and since alternating current could not be used, the only direct method of calibration was that of rapidly interchanged applications of different positive potentials. Fig. 5 shows the connections as applied for this purpose. *F* represents an electro-tuning fork, making 100 vibrations a second and *mnop* represent mercury contacts to which the terminals of the storage battery S_2 were connected. When the transfer switch T_1 was thrown downward, the condenser plates *C* and *H* were connected to the storage battery S_2 through the mercury contacts of the tuning fork. When the tines of the fork approached each other, the circuit was opened at *op* and closed at *mn* and there was a difference of potential of say 800 volts between the plates *C* and *H*, but when the tines of the fork separated the circuit was broken at *mn* and closed at *op*, and there was a difference of potential of say 400 volts between *C* and *H*. Thus two known positive potentials were interchanged between the plates *C* and *H* 260 times each second and a known variation of potentia- was maintained between the condensor plates by means of the storage battery and tuning fork with which to compare the unknown differences of potential produced by the glow tube. Hence the interchanging known potentials as thus employed for calibration purposes were applied to the plates very much as they occurred in actual practice when coming from the discharge tube, and they produced a very definite line on the screen *S*, the maximum and minimum of which could be read very distinctly on the scale. The calibration curve given in Fig. 6 shows the variations of potential as they actually existed when the connections to the battery were made to the tuning fork in this manner, the potential development thus obtained being very different in character from those obtained from the discharge tube. By means of the tuning fork the condenser method can be applied to the Braun tube for all interrupted discharges of one direction. It can be applied without the tuning fork to all discharges of alternating directions.

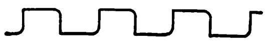


Fig. 6.

IV. METHOD OF OBSERVING THE DISCHARGE FREQUENCY AND THE SUCCESSIVE STAGES THROUGH WHICH THE POTENTIAL PASSES IN THE PROGRESS OF EACH DISCHARGE.

The measurements taken by means of the Braun tube and telescope as previously described determine simply the limits of potential differences. If, however, the fluorescent images on the screen *F* be observed by means of a rotating mirror, the lines will appear as curves, or waves, as seen in the charts. In most cases the complete wave is not visible, for only the rising portion and crest can be seen, while the falling portion is invisible. Each crest denotes a single charge and the number of these seen per second determines the frequency of discharge.

Moreover the form of the rising portion that is visible shows the various stages through which the potential passes from the beginning of each charge formation until the accumulated charge is discharged between the electrodes. For the elevation of the spot upon the screen at any instant measures the potential, and the horizontal projection of the line, taken in connection with the speed of the mirror, measures the duration of time required for each charge to accumulate.

Each complete period then may be considered as consisting of two distinct intervals, viz. that of charge accumulation, in which there seems to be no transmission of electricity between the electrodes, but in which the potential rises from minimum to maximum and the tube becomes charged; and that of charge transmission, in which the potential falls suddenly from maximum to minimum and the accumulated charge passes between the electrodes. This latter we may call the *true discharge*, and the mean rate at which the transmission takes place during this latter interval we have called the *true current intensity*. The true discharge takes place so rapidly that in most cases it leaves no line of light upon the mirror owing to the insufficiency of light, and the duration of the interval is denoted by a break in the visible line. The line, if seen during the true discharge, would differ but slightly from a vertical line. In a few cases such a line was actually visible faintly connecting the maximum to the minimum potential.

By means of this method, therefore, it is not usually possible to trace the potential variations which occur during the true discharge, but they can be plainly seen during the charge accumulation. It is also possible to determine with considerable accuracy both the frequency of discharge and the time required for the charge transmission, as well as to calculate the true current intensity.

Various conditions which affect the charge and discharge phenomena were examined at this time.

V. Description of Tests Made and Results Obtained.

(*a*) *Simultaneous Measurements of Potential by Means of Calorimeter and Braun Tube.*

Table II. gives the results of potential measurements of disruptive discharge made simultaneously by means of the calorimeter (apparatus *D*) and the Braun tube. The object of this series was to ascertain whether the results obtained by one method would agree with those obtained by the other, when applied to disruptive discharges. The potential measured was that produced by the discharge between the electrodes of apparatus *D*, the vacuum being varied as indicated in the table. Column 3 of the table gives the mean voltage as determined by heat measurements, column 4 gives the corresponding potential as measured directly by means of the Kelvin multicellular voltmeter, and columns 5 and 6 give respectively the maximum and minimum voltage as obtained by the Braun tube measurements, while column 7 is the numerical mean of 5 and 6.

It will be seen from this that the potentials obtained by the calorimeter method are very nearly the same as those obtained by the Kelvin voltmeter. The differences may be accounted for perhaps, by errors in measurement. They also lie between the maximum and minimum values obtained by the Braun tube, as would naturally be expected, but they are much larger than the numerical mean given in column 7. So great a difference as this cannot be attributed to errors of measurement, especially since the difference is always in the same direction. It may be remarked, however, that according to the potential curves, given later, the numerical mean of the maximum and minimum would probably be less than the actual mean. But the most important point to be noticed in these results is the fact that the potential never even approaches zero, but falls to a minimum only, which remains constant for the particular condition under which the test is made. The conditions of test seem to affect both the minimum and maximum potentials. This is referred to again later. The Braun tube method made it

Table II.

Potential of Disruptive-Discharge, as Determined Simultaneously by Means of Calorimeter and Braun Tube.

Test No.	Air Pressure in mms. 1	Galv. Deflection $k=38\times10^{-8}$. 2	Potential Determined by Means of				
			Calorimeter App. D. 3	Kelvin Voltmeter. 4	Braun Tube.		
					Max. 5	Min. 6	Mean. 7
1	4.9	1.05	391	381	416	224	320
2	1.8	2.15	418	425	544	240	392
3	1.7	2.22	401	417	480	223	352
4	1.7	2.23	406	413	480	240	360
5	1.7	1.75	400	413	480	225	352

possible to examine the phenomena in tubes of many forms and under many conditions which would not have been possible by means of the calorimetric method. Having reason for believing that the character of discharge was not the same for all tubes nor the same for any one tube under all different conditions, we made tests on various kinds of tubes, some of which are represented in Fig. 4, and varied the conditions for each different tube.

(*b*) *To Test the Effect Produced by Changes in Resistance and Air Pressure.*

Chart I. gives the results of a characteristic series of tests made upon discharge tube *E* for the purpose. The connections are represented in Fig. 3. The discharge was produced by a current from storage battery S_1 of 1,040 volts. A liquid rheostat *R* of very high resistance was placed in series with a tube *AB*; experiments proved that by varying the amount of this resistance the character of the discharge could be entirely changed. With a small resistance the discharge was always continuous and the image upon the fluorescent screen was a small round spot fixed in its position. For such conditions the curve in the mirror was seen to be a horizontal straight line at some definite constant potential, as represented in Chart I., tests number 1, 7, 8, 14 and 19. With a large resistance, however, the discharge became disruptive and the fluorescent image upon the screen was a thin vertical line varying in length according to the difference between the maximum and minimum potentials in the glow tube. Tests 3 to 6 are good examples of this. Accordingly tests were made with various resistances while the pressure was kept constant as shown in tests 1 to 8 inclusive. Then with a different air pressure the tests were repeated with the same series of resistances as nearly as possible, (see tests 7 to 13 inclusive). This was repeated for a number of different air pressures. In every case the potential measurements were first made and immediately afterward the curves were observed in the rotating mirror. In this way the potential limits were determined and the character of the discharge was plainly seen as to whether it was continuous or disruptive, and if disruptive, how great was the frequency and what stages of development the potential passed through at every

CHART I.

Changes in Resistance and Air Pressure.

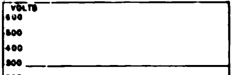
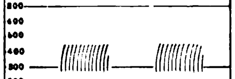
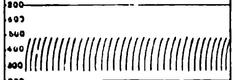
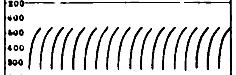
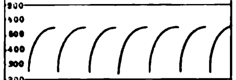
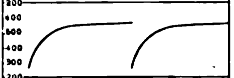
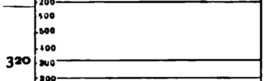
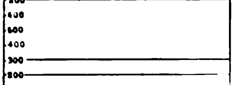
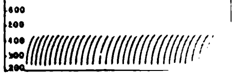
Test No.	Air Pressure.	Resistance in Circuit.	Galv. Defl. $K = 21 \times 10^{-6}$	Max and Min. Volts of Curves.	Potential Curves for Each Test, Representing Form, Amplitude and Approx. Relative Frequency.	Remarks.
1	2	3	4	5	6	7
1	3	1	21.3	284		Apparently a continuous discharge. Is stable and no breaks are visible in the line.
2	3	2	15.5	458 280		Unstable discharge. Fluctuates between continuous and disruptive, without change in external resistance. The glim is longest when the discharge is disruptive
3	3	3	8.9	488 270		Stable disruptive discharge. Discharge lines are distinct in mirror, but too numerous to count. Have form as here given
4	3	4	5.8	535 260		Frequency not so great as in Test 3, but greater than in Test 5.
5	3	5	3.4	556 264		Character of curves in Test 5 seems to be the same as in former tests. Seven lines visible in the mirror.
6	3	6	3.3	561 267		Only two lines can be seen in the mirror at a time in Test. 6, though in Test 3 they were too numerous to count.
7	1.07	1	12.6	320		The external conditions in Test 7 are the same as in Test 1, but the air pressure is less here. Discharge stable and continuous. Glim is very short.
8	1.07	2	8.5	328		Discharge is unstable in Test 8 Fluctuates between continuous at 328 volts and disruptive discharge with min at 245 and max. at 435 volts. Tests 8 and 9 are practically the same test, the discharge fluctuating spontaneously from one form to the other.
9	1 07	2	7.5	435 245		The glim in 8 is short, but in 9 it nearly covers the cathode. Tests 8 and 9 seem to correspond to Test 2, but with less air pressure.

CHART I.—*Continued.*

Changes in Resistance and Air Pressure.

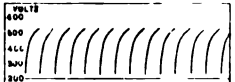
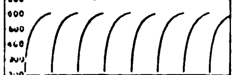
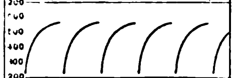
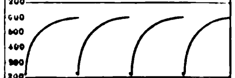
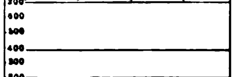
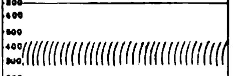
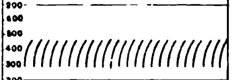
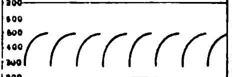
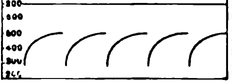
Test No.	Air Pressure.	Resistance in Circuit.	Galv. Defl. $K = 21 \times 10^{-6}$	Max. and Min. Volts of Curves.	Potential Curves for Each Test.	Remarks.
1	2	3	4	5	6	7
10	1 07	3	6.3	534 240		Stable disruptive discharge. The frequency here is less than in Test 9, and the amplitude is greater.
11	1.07	4	3.8	604 224		
12	1 07	5	2.4	560 224		The glim light does not cover the cathode in Tests 7 to 13 inclusive
13	1.07	6	2.0	592 216		In Test 13 the curves have a decided curl upward at the lower limit, but no connecting line is visible between the upper end of one curve and the lower end of the next
14	0 52	1	10.8	376		In Test 14*a*, hazy continuous horizontal band is seen in the mirror, with constant potential of 376 volts.
15	0.52	2	8.3	436 297		Stable disruptive discharge in Test 15. Frequency too great to count the lines in the mirror. Glim does not cover the cathode in Tests 14 to 18 inclusive.
16	0.52	4	3.8	458 290		The numerals in column 3, "Resistence in Circuit," indicate the amount of resistance that is placed in series with Battery S and the glow tube. No. 1 signifies the smallest resistence that can be obtained by the Liquid Rheostat, while No. 8 denotes the largest amount.
17	0.52	5	1.6	495 285		
18	0 52	8	0.4	500 283		The intervening numbers denote relatively proportional amounts. This applies throughout all the tests.

CHART I.—*Concluded.*

Changes in Resistance and Air Pressure.

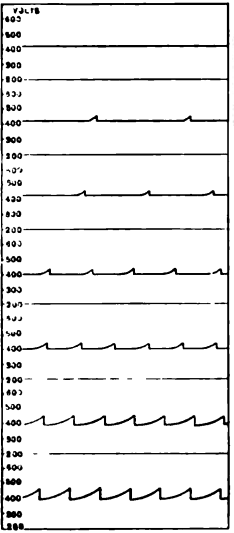
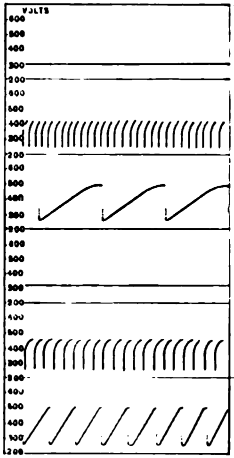
Test No.	Air Pressure.	Resistance in Circuit.	Galv. Defl. $K=21\times10^{-6}$	Max. and Min. Volts of Curves	Potential Curves of Each Test.	Remarks.
1	2	3	4	5	6	7
19'	0.25	6	1.4	426		The glim light is short Stable continuous discharge. As the resistance in the liquid rheostat is gradually increased from Resistance 6 in Test 19' to Resistance 7 in Test 20', the curves undergo the following changes as seen in Test 19', 19'', 19''' and finally Test 20' where the potential was again measured. As the resistance is gradually increased from Resistance 7 to Resistance 8 the interruptions become more frequent and the max. potential rises slightly. See 20'' and 20'''. With this low air pressure (0.25) the character of discharge as seen in Tests 19' to 21 is quite different from that of greater air pressure as seen in Tests 1 to 18 inclusive. Resistance 8 = two high-resistance liquid rheostats, are in series. A fine discharge-line is seen in all of these tests (19' to 21) connecting the max. to the min. potential. In all other parts the band is broad. The glim covers the cathode in Tests 20' to 21 inclusive, but not so in the previous tests.
19''	"	6+	"			
19'''	"	6++	"			
20'	"	7	1.4	448 408		
20''	"	7+				
20'''	"	7++				
21	"	8	0 3	476 408		

CHART II.

Changes in Capacity and Air Pressure. Tests all made at the Critical Point.

Test No.	Air Pressure.	Resistance in Circuit.	Condenser.	Galv. Defl. $K=42\times10^{-6}$	Max. and Min. Volts of Curves.	Potential Curves for each Test, Representing Form, Amplitude and Approximate Relative Frequency.	Relative Freq'cy.	Remarks
1	2	3	4	5	6	7	8	9
22'	0 53	3	Out	4.7	304			Continuous discharge which changes spontaneously to disruptive or vice versa. This condition we have called the "Critical Point" When the condenser is "out" (not connected) the discharge is as seen in Test 22' or 22'', but when the condenser is "in" (is connected) the discharge becomes that of 22'''. The ratio of frequency in 22'' to that in 22'' is 10 to 1. When the air pressure is reduced to 0.30 mm the discharge at Critical Point becomes that of Test 23', 23'' and 23'''. The ratio of frequency in 23'' to that of 23''' is 10 to 4. The glim light in 22''' and 23''' covers the cathode, but, not so in the other cases Notice the decided curl upward at the lower limit of the curves in Test 22''' and 23'''.
22''	"	"	Out	4.0	416 256		30	
22'''	"	"	In	4.4	496 256		3	
23'	0.30	4	Out	7 0	320			
23''	"	"	Out	6 5	464 256		20	
23'''	"	"	In	6.3	496 256		8	

discharge. The mirror was rotated as nearly as possible with uniform speed so that the relative frequency in the various tests was approximately seen. In the charts each horizontal space (except the one at the top) which we have called a horizontal "row" is devoted to a single test, and the test to which it is devoted is indicated by the numeral at the left. The vertical spaces we have called "columns" and each column is devoted to some particular phase of each respective test. The horizontal row at the top of the page tells what particular phase of the test each column is devoted to. Thus in Chart I., column number 1 tells the number of the test to which each row is devoted, and column number 5 gives the maximum and minimum potential obtained in each test, while column number 6 represents the potential curves for that test. Thus column number 5 shows that the curves of column number 6, test number 3, begin at a minimum of 270 volts and rise to a maximum of 488 volts, and the form of the curves in column number 6 shows the stages through which the potential passes. The curves are drawn on a scale which is common to all tests, the ordinates denoting potential and the abcissas denoting time. For want of space the potential from zero to 200 volts has been omitted from the charts, since in the tests the minimum potential was never found to fall below 200 volts. The bottom ordinate in each test-chart, therefore, denoted 200 volts, while the top one represents 700 volts. As nearly as possible the curves in each row represent the discharge lines as actually seen in the mirror both in form and relative frequency. The numbers in column number 5 then denote the upper and lower potential limits as measured by the curves in the same horizontal row in column number 6 and the number of lines drawn in the row in column number 6 denotes the relative frequency of discharge for that test, the mirror being kept as nearly constant as possible throughout.

Among the things learned from the experiments represented in Chart I. in which the resistance in the external circuit was varied, while other conditions remained unchanged, was the fact that a change in external resistance will change the character of discharge from continuous to disruptive or *vice versa* and also that there is one point where the resistance can be such that the discharge will fluctuate spontaneously from continuous to disruptive or *vice versa* without any external change in resistance; this may be called the critical point and is apparently the only condition that can be reproduced from time to time with approximate certainty.

(*c*) *To Test the Effect Produced by Changes in the Capacity of the Circuit at Various Air Pressures.*

Having reasons to believe that the character of discharge was altered by changes in capacity, experiments were made to test the supposition. For this purpose tube *F*, Fig. 4, was used in the same manner as *E* was used in the preceding experiments, except that the plates of a Kohlrausch condenser were connected to the electrodes of the tube by means of a switch in such a way that they could be connected or disconnected, quickly, at pleasure, without changing the speed of the rotating mirror. The tests were made at the critical point. That is while the charge was continuous and the condenser was disconnected (out), the external resistance was gradually increased until the critical point was reached and the measurements made, then the measurements were repeated with the condenser connected (in), the speed of the mirror being kept constant. The change in potential was easily determined and the character of the curves observed. Characteristic results are given in Chart II.

(*d*) *Changes in Capacity and Distance Between the Electrodes.*

To test the effect of variations in capacity and distance between the electrodes, measurements were made upon tube *H*, Fig. 4. This tube was so constructed that by applying a magnet externally to the iron portion *b* of the electrode *ac* the distance *cd* between the electrodes could be made any desired length. Results of a characteristic series of measurements are given in Chart III. All tests were made at the critical point, and with the exception that the resistance in the circuit had to be increased a little to produce the critical point, when the electrodes were further apart, the conditions were alike in all corresponding tests. The air pressure was one millimeter throughout the series.

CHART III.

Changes in Capacity and Distance Between the Electrodes.
All Tests Made at Critical Point on Tube H.

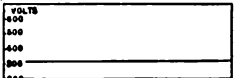
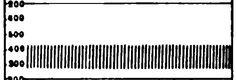
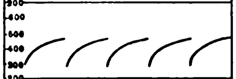
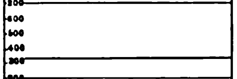
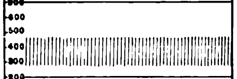
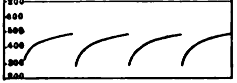
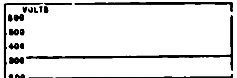
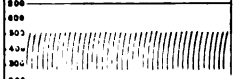
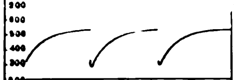
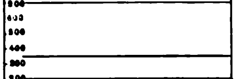
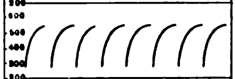
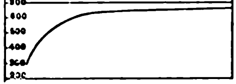
Test No.	Distance Between Electrodes in Cms.	Condenser.	Galv. Defl. $K = 42 \times 10^{-6}$	Resistance.	Max. and Min. Volts of Curves.	Potential Curves for Each Test, Representing Form, Amplitude and Approx. Relative Frequency.	Frequency.	Remarks.
1	2	3	4	5	6	7	8	9
24′	2	Out	18.1	3—	320			Glim light covers about $\frac{1}{10}$ of cathode. Discharge fluctuates at critical point as seen in 24′ and 24″. Glim covers about ½ cathode in 24″.
24″	2	Out	17.5	3—	432 272		?	Lines too numerous to count in 24″.
24‴	2	In	16.9	3—	470 290		5	Glim covers entire cathode and only 5 lines visible in 24‴. Discharge changes from 24″ to 24‴ spontaneously, simply by connecting "in" the condenser.
25′	5	Out	15.3	3	334			Glim covers about $\frac{1}{10}$ of cathode in Test 25. Test 24 differs from Test 25 respectively only in cms. distance between electrodes
25″	5	Out	14.2	3	456 278		?	Glim covers ½ of cathode. Lines too numerous to count Discharge changes from 25″ to 25‴ spontaneously, and from 25″ to 25‴ by connecting "in" the condenser.
25‴	5	In	14.2	3	490 292		4	Glim covers entire cathode and only 4 lines visible in 25‴.

CHART III.—*Concluded.*

Changes in Capacity and Distance Between the Electrodes.
All Tests Made at Critical Point on Tube H.

Test No.	Distance Between Electrodes in Cms.	Resistance.	Condenser.	Galv. Defl. $K = 42 \times 10^{-6}$	Max. and Min. Volts of Curves.	Potential Curves for Each Test, Representing Form, Amplitude, and Approx. Relative Frequency.	Frequency.	Remarks.
1	2	3	4	5	6	7	8	9
26′	10	3^{+}	Out	13.8	336			Glim light covers $\frac{1}{10}$ of the cathode in 26′.
26″	10	3^{+}	Out	13.1	512 272		40	Glim covers about ½ of the cathode in 26″ and 40 lines are visible in the mirror.
26‴	10	3^{+}	In	12.4	530 290		3	Glim covers the entire cathode in 26‴ and 3 lines are visible in the mirror.
27′	20	3^{++}	Out	7.1	352			Glim covers about ½ of the cathode in 27′.
27″	20	3^{++}	Out	5.7	560 272		8	Glim covers about $\frac{1}{8}$ of the cathode in 27″ and 8 lines are visible in the mirror
27‴	20	3^{++}	In	5.0	672 288		1	Glim covers entire cathode in 27‴ and one line is visible in the mirror A decided upward turn is seen at lower limit of curve.

(*e*) *Comparison of the Phenomena of Positive and Negative Discharge with Reference to Frequency and Capacity.*

Professor G. Wiedemann found (Elektricetät von G. Wiedemann, 4, p. 459), that with the current from an influence machine, and therefore of uniform intensity, the frequency was greater when the negative electrode was free and the positive connected to earth, than when the positive was free and the negative was connected to earth. That is to say, with uniform current a negative discharge gave a greater frequency than the positive. From this he assumed that the voltage varies inversely as the frequency, on the assumption that

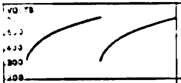
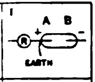
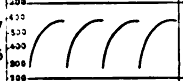
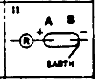
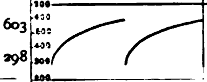
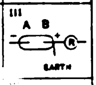
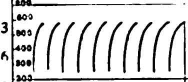
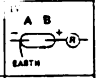
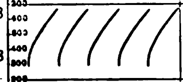
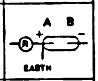
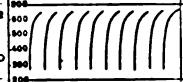
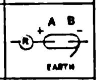
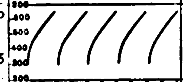
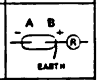
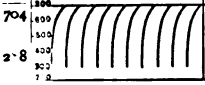
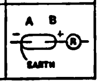
$$n = \frac{I}{CV}.$$

In other words that, if the frequency is decreased one half, the voltage should be doubled. This assumption must be true, of course, if the capacity remains constant. Professor E. Wiedemann and others have, at various times, obtained results some of which verify this law of frequency and some contradict it, and no satisfactory reason has been given for the discrepancy. Professor E. Wiedemann has suggested that perhaps the capacity does not remain constant. To ascertain whether this can be the case or not, two series of tests were made. Results of the first series are given in Chart IV. while those of the second are given in Chart V.

In both series the current was kept constant in all cases and no changes were made, except that of reversing the current through the tube and interchanging the earth connection. The connections for the first series are as shown in Fig. 3 with the exception that the earth could be instantly connected to the electrode A or B of the glow tube at pleasure by means of an independent switch. In this series four combinations were possible as shown by I., II., III. and IV. in column 8 of Chart IV., where R in column 8 denotes the liquid rheostat as indicated by R of Fig. 3, in series with the battery S_1 and discharge tube AB. In I. and II. the direction of the current was unchanged while the earth was connected first to A and then to B. In III. and IV. the current was reversed in direction while the earth was again connected first to A and then to B. With these combinations it was found that the frequency obtained

CHART IV.

To Test the Effect of Interchanging the Earth Connection, i. e., to Compare the Phenomena Produced by a Negative Discharge, with that Produced by a Positive, the Tests Being on Tube F, with 2.8 mm. Air Pressure.

Test No.	Distance Between Electrodes in cms.	The Negative Charge is on	The Negative Electrode is	Max. and Min. Volts of Curves.	Potential Curves for Tests, Representing Form, Amplitude and Approx Rel. Frequencies.	Ratio of Frequencies	Plan of Tube Connections.	Remarks.
1	2	3	4	5	6	7	8	9
28′	10	B	Free	603 309		1		No condenser was used in these tests. A medium resistance was used in series and left constant throughout. The only changes made were the interchanging of the earth connection and the reversing of the current.
28″	"	B	Earthed	597 276		2		
29′	"	A	Free	603 298		1		
29″	"	A	Earthed	593 256		5		
30′	40	B	Free	688 288		1		
30″	"	B	Earthed	672 270		2		
31′	"	A	Free	670 305		1		
31″	"	A	Earthed	704 2·8		2		

from the positive electrode, as in II. and IV., was always very much greater than from the negative electrode as in I. and III. These results are therefore directly opposite to those obtained by G. Wiedemann and are not in accordance with his law of frequency, for although the frequency is doubled in some cases the potential varies very little, if at all. It will be noticed, however, that in I. and III. the earth connection is made between the tube and the rheostat, while in II. and IV. it is not. It is possible therefore that the position of the rheostat may produce the change in frequency by changing the capacity of the circuit.

In the next series of tests the combinations were modified to avoid this difficulty. Fig. 7 shows the plan of connection for the second series and the four possible combinations are indicated in V., VI., VII. and VIII., column 10 of Chart V. The tests in this series were made as follows:

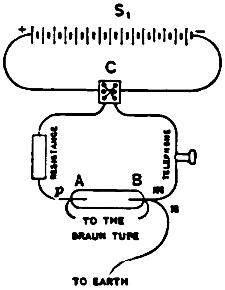


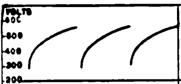
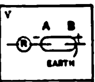
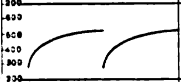
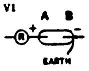
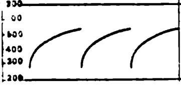
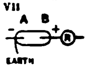
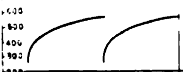
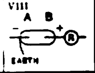
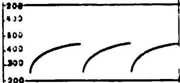
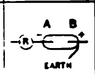
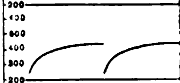
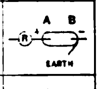
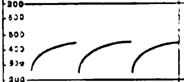
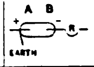
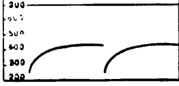
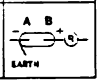
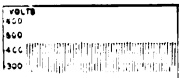
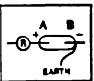
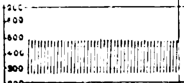
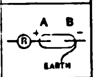
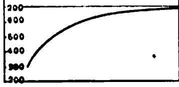
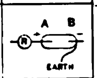
Fig. 7.

First two measurements were made with unchanged connections as in V. and VI., but with the direction of the current reversed in one of them, so that in V. there was a negative discharge from *A* while in VI. there was a positive discharge from the same terminal, all other conditions being unchanged. Then all of the circuit connections, except those connecting to the Braun tube, were removed from *A* and *B* and interchanged in position. That is, the connecting wire *p* was removed from *A* and connected to *B* while the wires *m* and *n* were removed from *B* and connected to *A*. With these interchanged connections two more measurements were made as before with the current first in the direct and then in the reverse direction through the tube. In other words in VII. there was a positive discharge from *B* while in VIII. there was a negative discharge from the same electrode, all other conditions being the same. Hence, VII. and VIII. are exactly the same as V. and VI., respectively, except that the discharge proceeds from the opposite electrodes. If then, there is any difference between the frequencies obtained in these four cases, or if the potential in any case is greater than in another it must be due, either to some difference in the electrodes, or to some intrinsic difference in the character of the positive and negative discharge. Apparently the difference does not lie in the electrode, for interchanging the terminals does not seem to produce any different effect. An examination of Chart V. will show, however, that in all cases, whenever the discharge is negative the frequency is decidedly greater than when the discharge is positive. This is in agreement with G. Wiedemann's results, but the law of frequency does not seem to be verified in this series, for if

$$n = \frac{I}{CV}$$

Chart V.

To Test the Effect of Changing the Earth Connection, i. e., to Compare the Phenomena Produced by a Negative Discharge with that Produced by a Positive; 1st, With Changes in Air Pressure; 2d, With Changes in Resistance, and 3d, With Changes in Capacity. All Tests made on Tube F.

Test No	Resistance in Circuit.	Condenser.	Air Pressure.	The Negative charge is on	The Negative Electrode is	Max. and Min. Volts of Curves.	Potential Curves for Tests, Representing Form, Amplitude and Approximate Relative Frequencies	Frequencies	Plan of Tube Connections.	Ratio of Max. Voltages.	Remarks.
1	2	3	4	5	6	7	8	9	10	11	12
32′	3	Out	3.8	A	Free	560 274		3		$\frac{560}{526} = 1.06+$	
32″	3	Out	3.8	B	Earthed	526 274		2			
33′	3	Out	3.8	B	Free	547 266		3		$\frac{547}{573} = 0.94$	
33″	3	Out	3.8	A	Earthed	573 266		2			
34′	3	Out	1.21	A	Free	449 245		3		$\frac{449}{443} = 1.01$	
34″	3	Out	1.21	B	Earthed	443 245		2			
35′	3	Out	1.21	B	Free	449 251		3		$\frac{449}{437} = 1.03$	
35″	3	Out	1.21	A	Earthed	437 251		2			
36′	2	Out	1.8	B	Earthed	449 267		ABOUT 150			The frequency in 36′ is too great to count and can only be estimated, but is plainly greater than it is in 36″ which is estimated at 100. Only one line in the curve is visible in the mirror in test 36‴.
36″	7	Out	1.8	B	Earthed	481 256		ABOUT 100			
36‴	"	In	1.8	B	Earthed	688 309		ONE			

is true, when the current is uniform, then if C is constant, n should vary inversely as V, which does not seem to be the case in these results. If the potential changes at all, it seems to increase with the frequency rather than otherwise. At any rate, even after making full allowance for errors in measurement, the potential does not vary inversely as the frequency. This, then seems to indicate that the capacity of the tube does not remain constant.

VI. OBSERVATIONS AND CONCLUSIONS DERIVED FROM THE RESULTS.

Facts which may be noticed by examining the charts, combined with the phenomena noticed in the progress of these investigations may be condensed into the following observations:

From Chart I. it may be noticed:

1. With sufficiently low resistance in the circuit the discharge is continuous, but when the resistance is increased sufficiently the discharge suddenly becomes disruptive; the frequency of discharge continues to decrease, and the maximum potential to increase, from that point on as the external resistance is increased.

2. If the low resistance, at which the discharge is continuous, is increased very slowly, a critical point may always be found where the discharge fluctuates between the continuous and disruptive form without any change in the external circuit. Simply touching with the finger a point here or there in the external circuit is sufficient to cause the discharge to change back or forth from one form to the other, or the change may occur without any point being touched, or without any external variation whatever being made. This apparent spontaneous fluctuation is probably due to slight changes in the capacity of the external circuit, which is very easily affected. The tests which follow seem to indicate this.

3. The glim light is always longer when the discharge is disruptive than when it is continuous. This is true even at the critical point. But the true current intensity is greater for disruptive discharge than for continuous and, as already known, the glim is always longer the stronger the current. These observations have been noticed in course of the experiment although the facts have not been so stated before.

4. The potential never falls to zero nor even near it but varies between a maximum and minimum at each interruption. Plotting the potential curves with the potential, as ordinates and the time as abcissas, it is seen that from the minimum point the potential at

first rises very abruptly, but as it approaches the maximum, especially in discharges of low frequency, the increase occurs but slowly and the curve becomes nearly a horizontal line near the upper potential limit. When the potential has fully reached the maximum it falls off so quickly that the path of the fluorescent spot upon the screen usually becomes invisible in the mirror. This sudden drop in potential evidently denotes the instant at which the real discharge between the electrodes takes place. The potential develops as it does when a condenser is charged until the discharge potential is reached. Apparently the discharge takes place only after the walls of the tube have been fully charged. That is, there is a silent discharge from the free electrode to the walls of the tube which gradually raises the potential. Then when the maximum potential is fully reached there is a sudden discharge from the walls and from the free electrode to the electrode which is connected to the earth. Such a manifestation was formerly observed in the like phenomena examined by E. Wiedemann and Lehmann. In this manifestation may be found the reason for the results of G. Wiedemann concerning the difference between positive and negative discharges, in which the existing velocity of the negative electrons plays an important part. That the potential drops suddenly the instant the discharge sets in, is in agreement with the results which Hittorf has previously found, namely, that it requires a higher potential to begin a discharge than to maintain it.

5. With the discharge proceeding always from the same positive or negative terminal, it is seen that as the frequency of discharge decreases the limits of potential differ more widely, the maximum potential increasing greatly while the minimum limit seems to drop slightly. Or conversely, the greater the current intensity, that is, the greater the number of discharges per second, the smaller the amplitude of potential variation becomes. The reason for this is that the shorter the time interval existing between discharges the greater is the number of free electrons then in the tube, and accordingly the greater the conductivity of the gas. From this it follows that there can be no definite fixed discharge potential or normal potential for disruptive discharges, but the value will vary with every varying condition that may exist.

6. In some cases, especially in Chart II., an upward turn is distinctly seen at the lower limit of the curve. That is to say, as the fall in potential approaches the lower limit the fluorescent line gradually becomes visible and when the minimum is reached, the bend from a downward to an upward direction is clearly seen. This plainly indicates the direction of the curve in the invisible portion, and shows that the potential does not fall at any time below the so called minimum. In other words, the potential drops most rapidly near the maximum and then more slowly until it reaches the lower limit, when it begins to rise again. The change in the curve from a downward to an upward direction, so clearly seen at the minimum point, plainly indicates the lowest limit of potential. This is also verified by the fact that the mean potential obtained by heat measurements and by direct voltmeter measurements as seen in Table II. lie between the maximum and minimum potential limits.

7. The minimum potential of disruptive discharge is seen to be lower than the constant potential of continuous discharge. This indicates that there are more free electrons in the gas during the instant of actual transmission in disruptive discharge than at any time during the continuous. This makes the conductivity greater and consequently the minimum potential lower in the former case than in the latter. In other words it indicates that the true current intensity during the short periods of active transmission in disruptive discharges is greater than the current intensity of a continuous discharge. In like manner it is seen from Charts I. to III., inclusive, that within limits, as the air pressure within the tube is decreased the potential of continuous discharge is increased.

8. The results given in Charts II. to III. show also that as the capacity of the tube is increased the maximum potential of disruptive discharge is raised and the minimum is lowered; also, the frequency is diminished.

9. As the air pressure is decreased the capacity of the tube is increased. This seems to be true, for in tests which were alike in all respects, except in air pressure, the results indicate that the tube had a greater capacity with a high vacuum than it had with a low one. An example of this is seen in tests 22″ and 23″, Chart II.

in which the air pressure was 0.5 mm. in the former and 0.3 mm. in the latter. Now, if C, I. N and V denote respectively capacity, current intensity, frequency and potential, then

$$\frac{C_1}{C_2}=\frac{I_1N_2V_2}{I_2N_1V_1}.$$

Supplying the corresponding values obtained in 22″ and 23″ we have

$$\frac{C_1}{C_2}=\frac{4\times 20\times 464}{6.5\times 30\times 416}=\frac{1}{2.2}\text{ nearly.}$$

That is, the tube has a greater capacity when the air pressure is small than when it is larger.

10. Results given in Chart III. show that the potential of continuous discharge rises slightly as the distance between the electrodes increases, as would be expected.

11. As the distance between the electrodes is increased the frequency of discharge decreases and the maximum potential increases. In other words, increasing the distance between the electrodes seems to have the effect of increasing the capacity of the tubes.

12. It is seen from these measurements that the minimum potential is not affected either by changes in capacity or distance between the electrodes.

13. Results given in Chart V. show that, other things remaining the same, the negative discharge has a higher frequency than the positive, though Chart IV. shows that the external circuit may easily be modified so that the positive discharge will have a higher frequency than the negative. In other words, the character of discharge within the tube is so intimately related to every external condition of the circuit, that any apparently slight modification without may entirely change the phenomena within. This being true the discrepancies between the results of G. and E. Wiedemann may easily be accounted for on this basis.

14. The results given in Chart V. do not verify the law

$$n=\frac{I}{CV},$$

since the potential does not in any case vary inversely as the frequency. On the other hand, they show that the capacity is not a constant quantity, but is different when the discharge is negative from what it is when the discharge is positive. Perhaps the explanation of this may be found in the difference that exists between the velocities of the positive and negative electrons.

15. In sending a disruptive current through a vacuum tube each period seems to consist of two very short intervals, the interval of charge accumulation and that of charge transmission. During the first interval the electrodes and walls of the tube become charged while the voltage rises from the minimum to the maximum potential. The various stages through which the potential passes during this first instant is denoted by the curved line as seen in the mirror, the first portion of which gradually curves away from the vertical and the latter portion is nearly horizontal. During the second interval, or instant, the true transmission of electricity takes place and is denoted by the break in the line indicating the drop in potential, as the voltage falls from maximum to minimum. The second interval is very short compared with the first. In other words, the time required for the true transmission of electricity between the electrodes is only a very small fraction of the total period. Apparently it is possible here to measure the duration of each interval, that is, not only to determine the frequency and time required for the charge to accumulate and the voltage to rise, but also to determine the duration of time required for the actual passage of electricity between the electrodes and the mean actual current intensity during that instant. Further tests are in progress for deriving these values.

Western University of Pennsylvania,
Allegheny, Pa., Jan., 1904.

ON THE USE OF NICKEL IN THE CORE OF THE MARCONI MAGNETIC DETECTOR.

By Arthur L. Foley.

THE magnetic detector of electric waves, described and used by Marconi,[1] consisted of a "core or rod of thin iron wires on which were wound one or two layers of thin insulated copper wire. Over this winding insulating material was placed, and over this again, another longer winding of thin copper wire contained in a narrow bobbin." One terminal of the inside winding was connected to earth, the other to an elevated conductor. The ends of the outside winding were connected to a telephone. A horseshoe magnet, suitably placed, was moved by clock work so as to cause a continuous change or successive reversals, of the magnetism of the iron core. Electric oscillations of suitable period appeared to reduce the effects of magnetic hysteresis, hence the magnetism of the iron core increased or decreased suddenly with each spark of the transmitter, inducing a current in the outer winding connected to the telephone. Marconi had (June, 1902) used this apparatus for some months in the reception of wireless telegraph messages over a distance of 152 miles, and with less power employed at the transmitting station than would have been required had he used a reliable coherer instead of the magnetic detector.

Marconi noticed that "the signals in the telephone are weakest when the poles of the rotating magnet have just passed the core and are increasing their distance from it, whilst they are strongest when the magnet poles are approaching the core." To obtain more definite results on this point I arranged to use a ballistic galvanometer instead of a telephone, and to take readings for various determined positions of the magnet and core.

The core, which was 5 cm. long, consisted of twenty-six pieces of annealed piano wire, .063 cm. in diameter. Over this was wound a single layer of two-hundred turns of silk insulated copper wire No. 36, giving a total diameter core and coil of approximately .4 cm. One end of the coil was connected to a vertical wire 200 cm. long, the other end was put to earth.

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[1] Note on a Magnetic Detector of Electric Waves, by G. Marconi. Proceedings of the Royal Society, Vol. LXX., No. 463, July 29, 1902.

The outer or secondary coil, consisting of one thousand turns of No. 30 copper wire, was wound on a wooden spool of such dimensions that the coil itself was 1.7 cm. long and .6 cm. in diameter (inside). The terminals of this coil were connected to a Rowland D'Arsonval galvanometer through a key arranged to short circuit the galvanometer after each throw of the needle. This brought the needle to rest very quickly, and permitted the position of the magnet to be changed without effecting the galvanometer.

The induction coil (one inch) of the transmitter was operated by a storage cell and was adjusted to give a 2-mm. spark between two small brass spheres, one connected to a vertical wire 200 cm. long, the other to earth. The distance between the transmitter and receiver was varied from two meters to twenty meters. The results given in this paper were obtained when the distance was made five meters. No effort was made to "tune" the circuits.

The magnet was made from a bar of steel 1.6 cm. square and 37 cm. long, bent so as to make a horse-shoe magnet about 16 cm. long with parallel legs 4.8 cm. apart. The primary and secondary coils were fastened in place on a board grooved and graduated so that the magnet could be slid back and forth in the same horizontal plane with, and in a direction at right angles to, the iron core, and placed at any desired distance from it. The graduations extended from 0 to 12 cm. zero distance corresponding to contact between the ends of the magnet and the core.

To get a reading, the galvanometer was first short circuited and the magnet placed in position. The short circuit was then broken, the transmitter operated as long as the deflection of the needle was increasing, and the throw observed.

Table I. gives the throws of the galvanometer for the given distances between the magnet and core:

A. When the magnet is placed 10 cm. from the core and moved one space nearer each successive reading.

B. When the magnet is placed in contact with the core and is moved one space farther from it each reading.

C. When the magnet is removed some distance after each reading and the transmitter operated before the magnet is placed in position for another reading.

D. When the magnet is turned over (the field reversed) between readings.

TABLE I.

Distance.	*A*	*B*	*C*	*D*
0.0 cm.	2.0 cm.			7.6 cm.
0.5	2.3	0.8 cm.	4.0 cm.	7.9
1.0	2.0	.9	3.2	6.1
2.0	1.3	1.0	2.0	3.5
3.0	.4	.9	1.2	1.6
4.0	.3	1.0	1.0	1.1
5.0	.2	.6	.5	.8
6.0	.1	.4	.3	.6
7.0	.0	.3	.2	.4
8.0	.0	.2	.2	.3
9.0	.0	.2	.1	.25
10.0	.0	.1	.1	.2

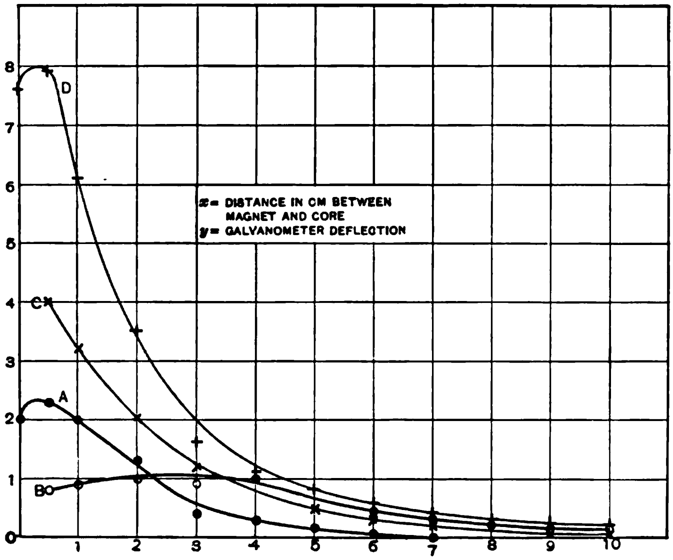

Fig. 1.

The data of Table I. are plotted in Fig. 1. A comparison of curves *A* and *B* shows that the sensitiveness of the magnetic detector depends upon both the distance and direction of motion of the moving magnet. When the magnet is near the core the detector is more sensitive when the magnet is approaching, but when some distance from the core the detector is more sensitive when the magnet is receding. Both curves indicate a maximum of sensitiveness at a distance from the core, the distance being less when the magnet is approaching than when receding.

Removing the magnet and operating the transmitter tended to demagnetize the core. Then when the magnet was placed in position and the transmitter again operated as in curve *C*, there was a relatively greater change in the magnetism of the core than was obtained under the conditions of curves *A* and *B*. Hence the deflections in column *C* are greater than those in *A* or *B*. It is evident that the relative change in the magnetization of the core would be greater still where the magnetic field is reversed after each reading, as in curve *D*.

Since nickel is more susceptible than iron in weak magnetic fields, and less susceptible in strong fields, it occured to the writer that a more uniform sensibility for varying distances between the moving magnet and core might be obtained by making the core of nickel.

Four cores were made, each one being 5 cm. long, approximately .4 cm. in diameter, and being wound with two hundred turns of No. 36 copper wire.

Core 1 consisted of 26 pieces of piano wire, .063 cm. in diameter.

Core 2 of 10 pieces of piano wire and 10 pieces of nickel wire, .082 cm. in diameter.

TABLE II.

Distance.	Core 1. Fe.	Core 2. Fe & Ni.	Core 3. Fe & Ni.	Core 4. Ni.
0 cm.	7.6 cm.	10.2 cm.	7.5 cm.	6.1 cm.
.5	7.9	9.5	7.5	9.0
1.0	6.1	8.0	7.2	8.9
2.0	3.5	4.6	4.0	4.7
3.0	1.6	3.0	2.0	1.35
4.0	1.1	1.7	1.0	0.7
6.0	0.6	0.5	0.4	0.35
8.0	0.3	0.2	0.2	0.2
10.0	0.2	0.1	0.1	0.1

Core 3 of 2 pieces of piano wire and 13 pieces of nickel wire.

Core 4 of 14 pieces of nickel wire.

Table II. gives the deflections at various distances between the magnet and each of the four cores, the magnet being moved one space at a time and having its poles reversed after each reading. The data for three of the cores are plotted in Fig. 2.

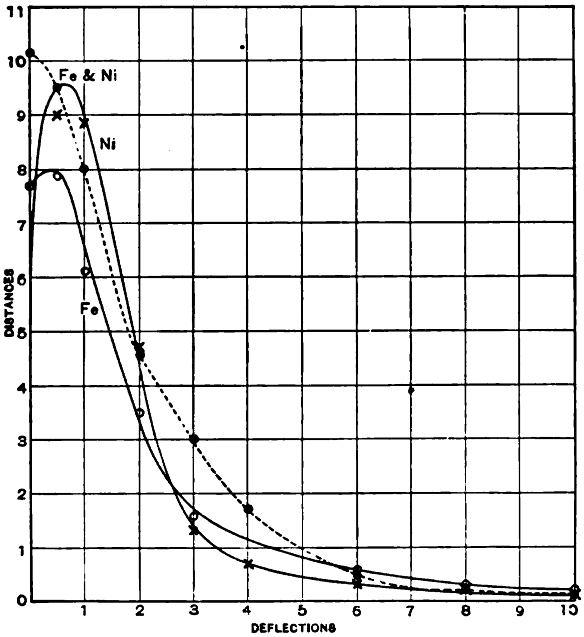

Fig. 2.

The sensitiveness of the detector with a nickel core was not very different from the sensitiveness when an iron core was used. Contrary to expectations, however, the sensitiveness with the nickel core appeared to be the greater in strong fields and with the iron core in weak fields. Both showed a maximum of sensitiveness at a short distance from the magnet, the maximum for nickel being the farther removed. The nickel core proved to be more sensitive than the iron core for distances up to 2.5 cm.

When the detector was worked with the mixed core of iron and nickel wires the deflections of the galvanometer increased as the magnet approached the core, even up to the point of contact. The curve (Fe and Ni, Fig. 2) lies above the Fe curve at all points and above the Ni curve at most points, showing that a mixed core consisting of annealed piano wire and hard drawn nickel wire, produced a more sensitive detector than was obtained by using a core of piano wire only.

The detector, gave small deflections of the galvanometer when I used an antimony core; also when I used a core of iron filings contained in a thin walled glass tube. In both cases deflections were obtained only when the magnet was near the core. A core of bismuth gave no deflection.

It is probable that the form of the curve of Figs. 1 and 2 depends upon other points than those considered in this paper, as for instance, the frequency and intensity of the oscillations sent out by the transmitter, and the annealing of the steel wires used in the core.

Since electric oscillations appear to "have the power of reducing the effects of magnetic hysteresis," it has occurred to the writer to test their effect upon the hysteresis loss of transformers, armatures, etc. Some experimental work on this subject has been done but I am not yet ready to announce results.

Physics Laboratory,
Indiana University, April, 1903.

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STUDIES IN LUMINESCENCE.

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

I. THE PHOSPHORESCENCE AND FLUORESCENCE OF ORGANIC SUBSTANCES AT LOW TEMPERATURES.

THE experiments here described are preliminary to a more extended study of phosphorescence and fluorescence at low temperatures, which will be, as far as possible, quantitative in character. Before undertaking quantitative experiments it seemed advisable, however, to test a large number of substances qualitatively, so as to determine which are best suited for further study.

The substances thus far tested are chiefly organic compounds of definite composition. Substances like white of egg, milk, ivory, etc., while in many cases possessing bright phosphorescence, seem too indefinite in their composition to be suited for exact work. Among the substances tested are several mentioned by Dewar;[1] but the behavior of the great majority of the substances included in the following tables has not to our knowledge been previously recorded.

The method of testing was briefly as follows: The substance was placed in a glass or porcelain dish in a dark room, and covered with liquid air, which was poured directly upon it. It was then illuminated by the light from a spark passing between magnesium terminals. Fluorescence, if at all intense, could be at once detected; while phosphorescence, if present, was observed after the spark had been stopped. By causing the light to pass through glass before reaching the specimen it was easy to determine, roughly, whether the effects were caused by the ultra-violet or the visible rays. Each substance was also tested at ordinary temperatures. In the case of about half of the substances the effect of X-rays was also tried, both at ordinary temperatures and when the substances were cooled by liquid air.

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[1] Dewar, Proc. Royal Soc., 55, p. 340; Proc. Chem. Soc., 10, p. 171; Proc. Royal Inst., 14, p. 665.

Previous experiments have shown that, as regards the effect of low temperatures on phosphorescence, bodies may be divided into at least three classes: (1) Substances in which the power to phosphoresce is increased by cooling; in this class are included substances for which phosphorescence is either weak or entirely absent at ordinary temperatures; (2) substances which are phosphorescent at ordinary temperatures, but which have this power diminished or destroyed at low temperatures; (3) bodies whose behavior, as regards phosphorescence, is apparently unaffected by cold.

We have found many examples of the first class and some examples of the third; but among the organic substances studied no example of the second class was found. Balmain's paint and the phosphorescent sulphides are the only substances tested by us which show diminished phosphorescing power when cooled.

Of the substances tested only 35 failed to show either phosphorescence or fluorescence when cooled to the temperature of liquid air. A list of these inactive substances is given in Table I., p. 361. In a few of these a trace of luminescence may have been present; but if so, the luminosity was so faint as to make it quite unlikely that the substances would prove interesting for further study. It should be noted that the frozen gases tested, viz., ammonia, sulphur dioxide, and ethylene, were contained in glass tubes, whose walls may have served to absorb the active rays of the exciting light.

The substances, 63 in number, which showed phosphorescence at low temperatures, but no fluorescence, are included in Table II. In this table are recorded (1) the approximate intensity of phosphorescence at ordinary temperatures as estimated by the eye, the most brilliant phosphorescence being indicated by the number 5, and the least bright by 1; (2) the intensity when illuminated, and observed, while at the temperature of liquid air, according to the same arbitrary scale as before; (3) the duration of phosphorescence: the number "5" in this column means a duration of several minutes, while "1" indicates a duration of one or two seconds; (4) the color of phosphorescence—in case no color is indicated the phosphorescent light was either white or only slightly colored; (5) the behavior of the substance, at the temperature of liquid air, when stimulated by X-rays.

In the great majority of cases the phosphorescence was due to the ultra-violet rays of the spark. This was shown by the fact that the effect of the spark in producing phosphorescence was either entirely or largely suppressed by the interposition of glass.

In considering the results recorded in Table II., one is struck by the fact that only a few of the substances showed luminescence at ordinary temperatures. The method of observation was not sufficiently refined to permit the detection of very faint phosphorescence, especially if of short duration. Observations made with the phosphoroscope would doubtless show that many of the substances here recorded as inactive at ordinary temperatures really possess a certain amount of activity. Yet the fact remains that the change produced by low temperatures in this property of matter is of a very radical nature.

In all cases where phosphorescence was found both at ordinary temperatures and in liquid air it was also observed throughout the whole intermediate range.

In several instances the greatest intensity of phosphorescence appeared to be at a temperature somewhat above that of liquid air. This was true for example in the case of phthalic anhydride, antipyrin, salicylic acid, arsenious oxide, benzoic acid, alcoholic solution of phenanthrene, coumarin, cetyl alcohol, quinine, and anthranol (Table IV.). Since the observations at intermediate temperatures were made during the rather rapid warming of the substance tested, it is, however, possible that the observed increase in brightness was due to the release of energy which had been stored in the substance. A striking instance of this phenomenon has been reported by Dewar in the case of ammonium platino cyanide.

Only ten substances were found which showed fluorescence at the temperature of liquid air without any noticeable phosphorescence. The behavior of these substances is recorded in Table III.

Of the substances tested the twenty that are included in Table IV. showed both phosphorescence and fluorescence at low temperatures. In these substances also the luminescence at ordinary temperatures was usually either slight or entirely lacking.

In the case of many substances the color of the phosphorescent light changed as the phosphorescence died away; in other words the different colors of the phosphorescent spectrum decayed at different rates. In some instances there could be little doubt that the observed luminescence was the resultant of two superposed effects, whose rates of decay differed widely. The color of the phosphorescent light was sometimes modified also by temperature, and in some cases by a change in the exciting rays. Some of the most striking cases of color change are mentioned below.

β Acet-naphthalid. — The initially yellow phosphorescence at − 186° C. changes to white as the phosphorescence dies out. The yellow tone is also lacking when the exciting light had passed through glass, while the white phosphorescence remains.

Anisic Acid. — The bright blue phosphorescence seen at low temperatures changes to a greenish yellow as the phosphorescence dies out. At higher temperatures no blue is seen in the phosphorescence, and at the same time the blue fluorescence seen at − 186° disappears.

Benzoic Acid. — The blue fluorescence seen at − 186° C. changes to greenish yellow at somewhat higher temperatures. The maximum phosphorescence seems to occur at a temperature somewhat above that of liquid air. The phosphorescence is initially bright green, losing this color as it dies out.

Calcium Benzoate. — The phosphorescence is at first bright blue, changing rapidly to white as it dies out. The blue fluorescence observed at − 186° C. ceases at slightly higher temperatures, and at the same time the phosphorescence loses its initial blue color.

Meta-carbol. — The phosphorescence at − 186° is initially a brilliant robin's egg blue. But the color is quickly lost as the phosphorescence decays, leaving behind a relatively weak but persistent white.

Metol-Hauff. — Initially blue. At the end of about two seconds the blue changes to green, which persists much longer.

Myricil Alcohol. — At − 186° C. the phosphorescence is a brilliant blue. At higher temperatures the blue changes to a fainter white, which is noticeable through a considerable temperature range.

Palmitic Acid. — Bright green, changing as the phosphorescence dies out to a persistent white.

Piperine. — Bright greenish phosphorescence. When the exciting light is passed through glass the greenish tint is no longer seen.

Phenanthrene (*Alcoholic Solution*). — Bright green phosphorescence of long duration, but changing to white as it dies out. The green part of the phosphorescence is suppressed when the exciting light passes through glass.

Pyrocatechin. — Brilliant green quickly changing to bluish white.

Tetra-chlor Phthalic Acid. — The fluorescence at − 186 ° C. is a bright robins' egg blue. At higher temperatures it changes to yellow.

In the case of the phosphorescent sulphides previous observers[1] have found that phosphorescence excited at ordinary temperatures is suppressed by sudden cooling. With substances of this class the phosphorescence produced by illumination at low temperatures is also small. Observations with benzoic acid indicate that the behavior of that substance is more complicated. Upon exciting phosphorescence at ordinary temperatures and then suddenly cooling in liquid air the phosphorescence is suppressed. The same is true if the substance is excited at some intermediate temperature and afterward cooled. Yet in the case of benzoic acid — contrary to the case of the sulphides — the phosphorescence *excited*, and *observed*, at low temperature is far more brilliant than at ordinary temperatures.

In several instances the luminescence of a solution was compared with that of a solid substance. Although the number of such cases is not sufficient to permit a general conclusion to be drawn, the tests show that important changes in the character of the luminescence are not unusual. Solid anthraquinone, for example, showed a brilliant yellow phosphorescence of short duration; while the frozen alcoholic solution[2] gave a bright bluish phosphorescence of long duration. The behavior of the solution resembled that of the solvent, but when the phosphorescence was compared with that of alcohol the latter was seen to be much weaker.

Phenanthrene offers another good illustration of the effect of solution. The solid showed blue fluorescence and yellow phosphorescence, both rather bright. When dissolved in absolute alcohol the fluorescence was no longer observed, while the phosphorescence was green instead of yellow, and of much longer duration. In the case of the solution the brightness was also much greater at a temperature somewhat above that of liquid air.

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[1] See Pictet, C. R., 119, p. 527; also Lumière, C. R., 128, p. 549, and Trowbridge, *Science*, 10, p. 244.

[2] Commercial methyl alcohol was used as a solvent.

An aqueous solution of piperidene behaved in the same way as the solid salt.

The influence of different solvents in modifying the luminescence phenomena at low temperatures was well brought out in the case of fluorescein. The brilliant fluorescence exhibited by this substance at ordinary temperatures also makes its behavior at low temperatures of especial interest. While solid fluorescein showed no luminescence, either when cold or at room temperature, the alkaline aqueous solution gave the usual brilliant fluorescence until cooled to the freezing point, when all trace of fluorescence disappeared. The temperature at which this sudden change occurred was measured by means of the resistance of a copper wire, and was found to be a few tenths of a degree below the freezing point of the solution. As a check upon this measurement the frozen solution was removed from its test tube for convenience in observation and slowly warmed in the air. Fluorescence was found to begin while the ice was still firm and before any indication of melting could be observed.

The behavior of fluorescein when used as an indicator in volumetric analyses has been explained upon the assumption that it fluoresces only when dissociated. When dissociation is prevented by making the solution acid, or by other means, fluorescence has been found to cease. Since dissociation can scarcely persist in the frozen aqueous solution we should therefore expect fluorescence to cease as soon as the solution solidifies. The apparently contradictory behavior mentioned above seems to result from the presence on the ice of minute drops of liquid which do not freeze until a temperature has been reached slightly below that at which the solution as a whole becomes solid. The change in concentration during the process of freezing naturally lowers the freezing point of those portions of the liquid which are last frozen.

In order to test this point the following experiment was tried.

The solution was introduced into a thick-walled glass tube of small bore, and after being sealed off at one end was connected with a Cailletet pump. The solution was then frozen by the application of cold brine. While still surrounded by the brine and at a temperature a little below the melting point, so that no fluorescence could be seen, pressures of nearly 200 atmospheres were applied by means of the pump. The frozen solution became fluorescent, and became inactive again when the pressure was released. The slight melting caused by pressure, without rise of temperature, restored to the solution its power to fluoresce. The sudden loss of this power is therefore not a temperature change, but is determined by the change of state from a liquid to a solid.

The behavior of fluorescein in alcohol solution is entirely different. A solution in absolute alcohol, rendered alkaline by the addition of dry caustic soda, showed a fluorescence only a little less intense than that of an aqueous solution. When this solution was cooled its fluorescence persisted and even at the temperature of liquid air was only slightly diminished. The frozen solution had the brittle vitreous character usually exhibited by solid alcohol. If the lumi-

Table I.

Substances showing neither Phosphorescence nor Fluorescence at — 186° C.

These substances are also inactive at ordinary temperatures.

Acetic acid, copper salt of.
Aceto-nitrile.
Aceto-acetic ether, copper salt of.
Ammonia (liquefied gas in glass tube).
Amido-azo-benzol.[1]
Azo benzene.[1]
Alizarin.[1]
Arsenic, As_2O_5 (faintly fluorescent at — 186° with X-rays).
Arsenic sulphide, As_2S_3.[1]
Didymium (aqueous solution).
Ethylene (liquefied gas in glass tube).
Formic acid, copper salt of.
Di-nitro-phenol.
Eosin, sodium salt of (solid).
Fluorescein (solid).
Gold chloride (solution).
Gutta percha.
Indigo.[1]
Iodol.
Magnesium oxide.
Mercuric-cyanide.
Nickel sulphate.
Phenanthraquinone.[1]
Phenyl iodide.
Phenyl mustard.
Pinine (lævo).
Pinine (dextro).
Prussian blue.
Quinone.[1]
Selenium (amorphous).
Sulphur dioxide (liquefied gas in glass tube).
Sulphuric ether.
Thorium oxide (white).
Tri-phenyl-guanadine.
Vanillin.

[1] Also tested with Röntgen Rays and found inactive.

TABLE II.

Substances which show Phosphorescence at — 186°, *but no Fluorescence.*

	18° C.	Behavior at — 186° C.			
	Intensity.	Intensity.	Duration.	Color.	X-rays.
Acetamide,	0	1		blue	0
Acetic acid,	0	2	4	blue green	
Acetophenone,	0	3	4	greenish	Ph(3)
Albumin (egg),	0	3		greenish-yellow	
Albumin (blood),	0	1			
Alcohol (absolute),	0	2	2		
Amyl acetate,	0	3	1		
Anthraquinone,	0	4	1	yellow	0
Anthraquinone, alcoholic solution,	0	4	4	bluish-white	
Antipyrine,	0	2	3		Ph(2)
Arsenic: As_2O_3,	0	1	1		0
Arsenic: As_2O_3, vitreous,	0	2			0
Arsenic: As_2S_3,	0	trace			0
Asparagin,	1	3	3	bluish	0
Benzaldehyde,	0	1	4		Ph(1)
Benzophenone,	0	3	2		Ph(2)
Camphor,	0	1			0
Carbostyril,	0	3	2		0
Casein,	0	1		bluish	
Cetyl alcohol,	0	5	4	bluish	
Citric acid,	1	3	3	greenish	
Coumarin,	0	1	2		
Diogen,	0	1	1		
Erythrite,	0	3	2		
Eucalyptol,	0	faint			0
Fusel oil,	0	3	3		
Glucose,	0	2	3		
Hydrogen peroxide,	0	2	3		
Hydro-azo-benzene,	0	1	2	greenish	0
Hydroquinone,	0	3	3	greenish	
Limonene (dextro),	0	1	1		
Malachite green (leuko compound),	0	3	3	greenish	
Menthol,	fl(trace)	3	3		0
Meta carbol,	2	5	3	green	
Methyl-amine hydrochloride,	0	3	3		0
Metol-Hauff,	0	4	1	blue	
Myricil alcohol,	fl(trace)	5	3	blue	
Napthalene,	0	1			Fl(1)
Palmitic acid,	0	4	3	green	

TABLE II.—*Continued.*

Substances which show Phosphorescence at —186°, but no Fluorescence.

	18° C.	Behavior at —186° C.			
	Intensity.	**Intensity.**	**Duration.**	**Color.**	**X-rays.**
Phenanthrene[1] (alcoholic solution),	0	5	4	green	
Phenolphthalein (alkaline aqueous solution),	0	3	3		0
Phenolphthalein, alcoholic solution,	0	3	3	blue	
Phenyl acetic acid,	0	5	3	white	Ph(3)
Phenyl propiolic acid,	fl. (trace)	1			
Phenyl-thio-carbamide,	0	1	2		
Phenyl-thio-methane,	0	1	2		0
Phthalic acid,	2 yellowish	3	2	greenish yellow	Ph(3)
Phthalic anhydride,	2 greenish	3	2	greenish	Ph(1)
Phthalic acid (iso-),	1 bluish	4	3	blue	0
Phthalic acid (tere-),	0	5	4	blue	0
Phosphorous pentoxide,	1	3	3		
Piperidene,	0	5	3	greenish	0
Pyradine,	0	1			
Pyrocatechin,	1	5	4	green	
Quinine (alkaloid),	0	3	2		0
Quinine sulphate (solid),	0	3	2		0
Quinoline,	0	2	3		0
Salicylic acid,	fl. (trace)	1	3		Ph(1)
Thio-carb-analide,	0	1			
Thiophene,	0	3	2		0
Theo-urea,	0	faint			0
Tolidol (Pfabe),	0	4	3	bluish	

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[1] For solid phenanthrene see Table IV.

TABLE III.

Substances Showing Fluorescence at Low Temperatures, but no Phosphorescence.

	18° C.	Behavior at —186° C.		
	Intensity.	**Intensity.**	**Color.**	**X-rays.**
Acridene.	0	4	green	
Carbazol.	2	3	blue-violet	0
Cyanin (alcoholic solution).	0	4	red	fluorescence (1)
Eikonogen.	0	3	purple	
Fuchsin (alcholic solution).	0	3	red	
Napthoic acid.	3	5	blue	
Piperine.	0	5	blue	
Uranium Nitrate.	Fluorescence not decreased by cold.			
Uranyl fluorid-fluor-ammonium.	4	4	green	
Uranium oxide (yellow).	0	3	greenish	

TABLE IV.

Substances showing both Phosphorescence and Fluorescence at — 186° C.

		18° C.	Behavior at —186° C.		
		Intensity.	Intensity.	Duration.	Color.
β-Acet-napthalide.	Ph	0	3	3	yellow
	Fl	2	3		purple
	x	—	—	—	
Aceto acetic ether.	Ph	0	3	3	white
	Fl	0	1	—	bluish
	x	0	0		
Acridine sulphate (solution).	Ph	0	1	2	
	Fl	0	1		
	x	—	—	—	
Anisic acid.	Ph	1	5	2	blue
	Fl	1	3		blue
	x	—	—		
Anthracene.	Ph	0	1	3	white
	Fl	4	4		blue
	x	trace	trace		
Anthranol.	Ph	0	3	1	yellow
	Fl	0	4		lemon yellow
	x				
Benzoic acid.	Ph	1	3	3	green
	Fl	0	3		blue
	x	fl. (trace)	phos. (4)	4	
Calcium benzoate.	Ph	1	3	3	blue
	Fl	0	3		blue
	x	trace	phos. (3)		white
Dianthracene.	Ph	0	3	2	yellow
	Fl	2	4		blue
	x	—	—	—	
Dimethyl dianthracene.	Ph	0	1	3	
	Fl	trace (?)	2		greenish
	x	—	—	—	
Diphenyl methane.	Ph	0	5	4	greenish yellow
	Fl	3	3		purple
	x	0	0		
Ethyl carbamate.	Ph	0	4	3	
	Fl	0	2		
	x	0	0		
Imogen.	Ph	0	1		
	Fl	trace (?)	4		violet
	x	—	—	—	

TABLE IV.—*Continued.*

Substances showing both Phosphorescence and Fluorescence at — 186° *C.*

		18° C.	Behavior at—186° C.		
		Intensity.	Intensity.	Duration.	Color.
Mellite.	Ph	2	3	1	purple
	Fl	2	4		purple
	x	0	faint		
Mellitic acid.	Ph	trace	5	3	bluish
	Fl	0	3		blue
	x	—	—	—	
Methyl salycilate.	Ph	0	1	2	
	Fl	0	4		blue
	x	0	trace		
Oxalic acid.	Ph	0	1	2	white
	Fl	0	2		violet
	x	—	—		
Phenanthrene.	Ph	0	4	2	yellow
	Fl	2	4		blue
	x	2	3		
Quinine sulphate (aqueous solution).	Ph	0	3		
	Fl	4	4		blue
	x	—	—		
Stearic acid.	Ph	0	5	1	green
	Fl	1	0		
	x	—	—		
Tetra-chlor phthalic acid.	Ph	0	3	2	
	Fl	0	4		blue
	x	0	5 (Fl.)		white
Tri-phenyl methane.	Ph	0	3	4	white
	Fl	2	2		blue
	x	0	0		

nescence of fluorescein is due to its dissociation we are thus forced to conclude that dissociation is still possible in solid alcohol at a temperature of — 186° C.

Instances are not lacking where substances that are closely related chemically behave in a similar manner as regards their luminescence at low temperatures. Benzoic acid and calcium benzoate offer a good illustration. The various members of the phthalic acid group also show a general similarity in their behavior. But attempts to trace a general relation between luminescence and chemical structure have not been successful.

SOME FURTHER OBSERVATIONS ON THE RADIATION PRODUCED IN AN ALTERNATING CONDENSER FIELD.

By Fernando Sanford.

In an article published in the Physical Review of December, 1903, Vol. XVII., p. 441, the present writer described some experiments which had been made on a form of radiation which is given off from the kathode of an air condenser connected to the terminals of an induction coil. It was shown that this radiation is capable of refraction, total reflection and polarization, but when the article was written its wave-length had not been measured. Since that time I have succeeded in measuring the wave-length of the radiation from several metals and have made some observations which enable me to explain some of the phenomena which were not before understood and to correct an erroneous conclusion as to the two kinds of radiation which were supposed to be sent off from metal plates placed in the field of the condenser.

The wave-length measurements were made by means of a Wallace celluloid replica of a Rowland plane grating having 14,438 lines to one inch. This grating was found to be fairly transparent to the radiation and to give definite spectra of the first order. The grating was placed over a slit about 3 mm. wide cut in a hard rubber screen which was placed between the source of the radiation and a photographic plate. The distance of the grating from the sensitive plate was, in the various experiments, from 4 cm. to 5 cm. This distance gave a displacement of the first diffracted image of the slit of from 8 mm. to more than 1 cm. The bands were generally sharply defined in the photographs, indicating that the radiation was virtually all of one wave-length from a given metal, and their displacement could be measured to within two or three tenths of a millimeter. The distance between the grating and the sensitive plate could be measured with a still higher percentage of accuracy, so that the error of measurement of the wave-length ought not to exceed four per cent. As a matter of fact, four different measurements of the wave-length from copper were made at different times using different copper strips as radiators and with different distances between the grating and the plate with a maximum difference in the four measurements of only 1 per cent. This close agreement must be regarded as accidental, but it is believed that the measurements are in general accurate to within four per cent.

The wave-lengths so far determined are as follows: For the radiation from aluminum and from silver, $\lambda = 350\,\mu\mu$. For the radiation from copper $\lambda = 372\,\mu\mu$ and for the zinc radiation $\lambda = 377\,\mu\mu$. As predicted in the preceding paper, this radiation is in the ultra-violet part of the spectrum and only a short distance beyond the visible spectrum.

No difference was found in the wave-length of the radiation from a piece of sheet copper when it was connected to the kathode of the induction coil and when it was insulated between the plates of a tinfoil condenser and gave off the radiation by induction. This observation contradicts one of the conclusions of the former paper concerning two kinds of radiation from a metal plate when insulated in the condenser field. The preceding paper mentioned the fact that when a strip of sheet metal was used as the radiator and an opaque screen with a slit was placed between the radiator and the sensitive plate two images of the slit were regularly formed on the plate, and that when a prism was placed across a part of the slit these two images were sometimes differently refracted. In the experiments where the radiating plate was connected directly to the kathode but one image of the slit was produced, and reasons were given for believing that these two images were produced by reflected and induced radiation. A further attempt to trace the origin of the two images has shown that they were due to the radiation from the two opposite edges of the metal strip. Even the earliest experiments in coin photography showed that the intensity of the radiation from the edges and convex surfaces of the coins was greater than from the plane faces, and this fact was mentioned in the paper on "Some Experiments in Electric Photography" in the Physical Review, Vol. II., p. 60, but this difference was not thought to be great enough to account for the phenomenon of the double image, though it was several times suspected to be the cause. The experiments with the radiator connected to the kathode seemed to exclude this explanation, but in those experiments a larger radiator was used and it was arranged so that only the radiation from the central part of the plate could reach the sensitive plate through the slit.

Later experiments have shown that when a thin piece of sheet metal is used as a radiator nearly all the radiation is from its edges. This radiation is diffuse, and apparently goes off in one direction nearly or quite as well as in another. Accordingly when a narrow strip of sheet metal was used as a radiator, as described on page 451 of the former paper, each edge served as a line source of radiation and two images of the slit were produced. Since the radiation from the two sources passed through the prism at different angles of incidence their deviation by the prism was different, and accordingly there seemed to be two kinds of radiation having different refractive indices. Many experiments have since been made with radiators of various width, both connected to the kathode and insulated in the condenser field, and there can be no doubt of this being the true explanation of the two images of the slit. In the latest experiments the radiating plate has been placed horizontal between the two horizontal condenser plates with one edge in front of and parallel to a horizontal slit in the opaque screen. With this arrangement only one image of the slit is produced and a narrower slit can be used than in the former experiments.

The sharp lines of separation between the radiations from the two radiating surfaces when separated by the glass prism as shown in the photographs on pp. 446 and 447 of the former paper are also explained by this phenomenon. When feeble radiators, as wood, paper, mica and glass are used, the principal source of radiation which reached the photographic plate was the edge of the radiating strip nearest the prism. The other edge of the strip was so far away that its effect upon the central part of the photographic plate was inappreciable in the photograph. When a metal plate was used as a radiator the radiation from its farther edge was still strong enough to be appreciable on the part of the plate which also received the radiation from the wood or paper on the other side.

The same phenomenon likewise explains the fact that when a window was cut in the top of the box camera and covered with the metal kathode the intensity of the radiation upon the sensitive plate beneath was not sensibly greater than when the whole box was covered by the *papier maché* slide. This was due to the fact that but little radiation was sent off rom the central part of the kathode plate which was placed over the window.

To sum up the observations to the present time, it may be said that when the terminals of an induction coil are connected to the plates of an air condenser and the current is interrupted in the primary coil the kathode plate gives off a radiation which possesses many, if not all, the properties of ordinary ultra-violet light. The wave-length of this radiation differs when the kathode plate is made of different metals, and for the metals aluminum, silver, copper and zinc it lies between 350 $\mu\mu$ and 380 $\mu\mu$. If a plate of metal or other substance be placed between the condenser plates it gives off the same radiation as when joined by conducting wires to the kathode, but with less intensity. In the case of a copper plate between tinfoil condenser plates this induced radiation has the same wave-length as when the copper plate is made the kathode of the condenser. Every body which has yet been tried may serve as a source of this induced radiation.

Stanford University,
February 6, 1904.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THE HALL EFFECT IN THE ELECTRIC ARC.[1]

BY C. D. CHILD.

IF two carbon pencils are so placed in an arc that there is little or no potential difference between them, a potential difference is produced by creating a magnetic field about the arc. This may be as high as 1.5 volts. It appears to be similar to the Hall effect in metals, and if it is this effect, it would show that the negative ions have a velocity enormously greater than that of the positive.

The effect can not be produced by blowing the arc to one side, nor by moving the carbon pencils to one side of the arc. Rapidly reversing the field and with each reversal reversing the connections to the voltmeter does not diminish the effect.

The effect decreases with decreasing strength of the field. Changes in the current through the arc and in the length of the arc do not appreciably influence it.

Putting salts in the arc diminishes the drop of potential at the anode and it also diminishes the effect here studied. With KNO_3 the anode drop becomes as small as the cathode and with it the potential difference between the two pencils becomes approximately zero.

However, in a vacuum where the pressure is approximately 1 cm. of mercury the effect also disappears and here the ratio between the drop at the anode and that at the cathode is nearly the same as in air at normal pressure. With an enclosed arc the effect is the same as in air. Diminishing the pressure of air produced no great change in the observed potential difference until a pressure of 20 cm. was reached. Between that and 10 cm. the effect was greatly diminished, and between 10 cm. and 1 cm., as far as could be observed, it entirely disappeared. Though the ratio between the anode and the cathode drop is not greatly changed, they each separately decrease, the principle change being between pressures of 20 cm. and 1 cm.

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[1] Abstract of a paper presented at a meeting of the Physical Society held on February 27, 1904.

The effect, therefore, is not diminished by any change in the ratio between the anode and cathode drop in potential, but as far as has now been observed it decreases when the voltage between the terminals of the arc decreases, becoming inappreciable when this becomes less than about 30 volts.

No definite explanation can at present be given of the observed phenomena.

NEW BOOKS.

Thermodynamik. Sammlung Schubert, xxxix. By Dr. W. VOIGT, Professor der theoretischen Physik an der Universität Göttingen. I. Band. Einleitung: Thermometrie, Kalorimetrie, Wärmeleitung. — Erster Teil: Thermisch-mechanische Umsetzungen. Mit 43 Figuren. 13 x 19 cm.; pp. xv + 360. Leipzig, G. J. Göschensche Verlagshandlung, 1903. Price, cloth, 10 marks.

It is not improbable that the best way to present the subject of thermodynamics is to give an account of its history — to show how, step by step, difficulties arose and were overcome, until the present beautiful body of theory was attained. Yet there is much to be said in favor of a more deductive treatment. On this plan, the first and second laws of thermodynamics may be established by inductive reasoning, the criteria of equilibrium and of stability be obtained through formulation of the spontaneous dissipation of work-availability, and from this basis the differential theory of the subject be developed in an orderly manner, and illustrated by such approximate integral theory as is at present possible. This is an interesting and instructive method, and it has the advantage of introducing the absolute temperature without any appeal to the properties of those overworked hypothetical substances, the ideal gases.

In the present work, Voigt has followed neither the one nor the other of these two plans. In his treatment the influence of the historical method is noticeable, for the theory of the subject is approached through the properties of ideal gases. The text of the present first volume is arranged in four chapters and an introduction. The introduction discusses thermometry, calorimetry, and heat-conduction. In the first chapter, an outline of the elements of the mechanics of a particle and of a system of particles is made to lead up to recognition of the equivalence of work and heat. The second chapter works up the thermodynamics of ideal gases. In the third chapter the second law is developed for bodies whose states of thermodynamic equilibrium are determined by two independent variables; and in the fourth the principles of thermodynamics are applied to systems whose states are determined by any number of variables. This concludes the volume and the first part of the work. Subsequent parts are to deal with chemical processes and changes of state of aggregation, electromagnetic actions, and applications of the principles of thermodynamics to radiation phenomena.

It is thus apparent that the treatment is given a wide scope. This is doubtless the excuse for the inclusion in the introduction of thirty pages on the theory of the conduction of heat. Some of the space so taken might better have been occupied by a clear explanation of how it is that the laws of Boyle and Gay-Lussac lead to the scale of temperatures of the ideal-gas thermometer. The brief statement in the text is not clear. The laws in question are not even stated separately. In the section on calorimetry the idea of a quantity of heat is introduced by means of the caloric fluid hypothesis. This *interpretation* of a certain class of facts is well enough as a matter of history, yet in this age of the world it should be emphatically pointed out that by a "quantity of heat" is *meant* the work value of a definite kind of change of the state of a body. It is to be noted at this point that Voigt employs Carl Neumann's hook-shaped d to indicate an inexact differential expression. This is, of course, a matter of no moment; yet the reviewer is grieved to see Voigt's own admirable notation $d'Q$ abandoned in favor of Neumann's impracticable idea. Apart from these details, Voigt's discussion of thermometry and calorimetry can only be commended.

In Chapter I., "The Equation of Energy and the Mechanical Equivalent of Heat," the mechanical principle of the conservation of energy is derived. Then, from the experimentally established equivalence of work and heat, it is concluded that additions of work and heat to a body "increase the work-availability, the energy, of the body," and the first law of thermodynamics is written down. The relation of this law to the impossibility of a "perpetual motion of the first kind" is discussed, a half dozen methods of determining the mechanical equivalent are described, and the law is applied to the heat-development of a falling meteor and to the Mayer and Helmholtz theories of solar-heat. It is not made clear that the "mechanical equivalent" is the specific heat of water.

We now come, in Chapter II., to the thermodynamics of ideal gases. Here preference is throughout given to volume and pressure as independent variables. By the "absolute teperature" θ is meant the temperature-reading of the ideal-gas thermometer. Reversible changes of the state of a homogeneous body under uniform pressure, in particular reversible isometric, isobaric, isothermal, adiabatic, and isodynamic paths, are described. The existence of a family of reversible adiabatic paths is gotten at by writing the heat equation in the form

$$d'\Omega = \Omega_1 dV + \Omega_2 dp = 0,$$

which, being always integrable, leads to a relation

$$f(V, p) = H,$$

where H is the parameter of the family of adiabatics. Hereupon we find

$$d'\Omega = \varphi(H, \theta)dH + \varphi'(H, \theta)d\theta,$$

or, since $d'\Omega$ varnishes for constant H,

$$d'\Omega = \varphi(H, \theta)dH,$$

a result that is not calculated to help the beginner much. Now the existence of ideal gases is assumed, and it is shown that, for the differential of the energy of the mass M,

$$dE = M\gamma_v d\theta.$$

The argument is clumsy, because of the selection of V, p as state-variables. Then, by an untransparent calculation that to a beginner could seem only a juggling with equations, we finally find, after one hundred and twenty-two pages,

$$d'\Omega = \theta dH.$$

Next, the form of $H = f(V, p)$ is found; it is shown that over a reversible cycle $\int(d'\Omega/\theta) = 0$; and H is termed the entropy of the ideal gas. The remainder of the chapter is concerned with the ratio γ_p/γ_v of the specific heats, an extensive geometrical and physical study of curves of the form $V^\kappa p = f$, a detailed examination of various reversible cycles with ideal gases, and applications to convective equilibrium in the earth's atmosphere and in a gravitating gaseous sphere.

After nearly two hundred pages of text, Chapter III. takes up the general examination of the thermodynamics of bodies whose states are determined by two variables. From the fundamental principles of Clausius and of Thomson it is concluded that the efficiency of a Carnot cycle is independent of the working system, and the formulation $d'\Omega = \theta dH$ is established. No reference is made to the clarifying principle that only processes that will spontaneously occur can be utilized as compensation for the doing of work. The laws of thermodynamics are now applied to yield Maxwell's "thermodynamic relations" in p,v, v,θ, p,θ, and θ,η. The relations in v,η and p,η are omitted. Further formulations obtained are those for the specific heats and for the heat-differential, in the same pairs of variables. A short sketch of the properties of the "first and second thermodynamic potentials" (the free energy and the thermodynamic potential) is added.

A section on liquids and solids gives certain special applications of the thermodynamic equations to these states. On the whole the treatment is good, yet one is surprised to find that in the energy equation in volume and temperature,

$$de = \gamma_v d\theta - \left(p - \theta\frac{\partial p}{\partial \theta}\right) dv,$$

the term in dv is asserted to represent an absorption of work unaccompanied by transfer of heat. Surely this is nonsense. It seems to have been assumed that $\gamma_v d\theta$ is the total absorption of heat.

The heading of a section on "actual" gases is disturbing, since we have been so confidently assured of the existence of gases ideal "*in voller Strenge.*" The section gives a good treatment of the porous-plug experiment, and of the theory of Linde's refrigerating machine. Up to this point (for 240 pages) the temperature has appeared in all formulas as the temperature $\theta = pv/B$ of the ideal-gas thermometer. Apparently the appearance of "actual" gases is making trouble, for now Thomson's scale of absolute temperatures is taken up. The scale is defined, and it is shown how the results of work with the porous-plug may be utilized for the correction of the scale of a gas-thermometer. A section on the increase of the entropy of an isolated two-variable system during spontaneous change, and one on the thermodynamic behavior of a stressed cylindrical solid, complete the chapter.

The closing chapter, on the thermodynamics of bodies whose states are determined by any number of variables, need not be discussed; since the character and plan of the book should be sufficiently gauged from what has already been said. It seems to the reviewer that here, as elsewhere, the treatment is characterized rather by command of detail than by breadth of view.

The work appears in the *Sammlung Schubert*, a series of text-books on various topics of pure and applied mathematics. The mechanical execution is not what it should be, none of the books of this series are very easy to read. The proofreading, however, has been well done; and the author has done what he could to relieve the eye, by breaking the text into short articles with topical headings. This is a distinct help. Very few references to the original literature are given. The volume is dedicated to Lord Kelvin. J. E. TREVOR.

Elementary Applied Mechanics. By ALEXANDER & THOMSON. The Macmillan Co., New York, 1902.

Starting with a brief presentation of the subject of lineal stress and strain the first chapter of this book includes also a discussion of elasticity and resilience. These subjects are very clearly presented and thoroughly prepare the reader to understand these terms as used in the analytical discussions which follow in the body of the book. Chapter 2 treats of internal stress and strain, simple and compound. Chapter 3 is devoted to Rankine's method of the ellipse of stress, giving the direct and inverse problems and illustrating them by photographs of a moving model. Next follow Chapters 4 and 5 treating the practical application of the foregoing discussions to the stability of earth work and the scientific design of masonry retaining walls. These first 5 chapters form as it were the first division of the book.

It should be noted here that the authors make and maintain a careful distinction between the terms strain and stress, the first invariably denoting distance, the latter force. The term strain always means the stretch due to a tensile stress or the shrinkage due to a compressive stress. The use of these terms in this way is rigidly adhered to throughout and leaves no lingering doubt in the mind of the reader as to the appropriateness of such a distinction.

Beginning with transverse stress in Chapter 6 the next eight chapters to Chapter 14 inclusive are taken up with a discussion of the different methods of loading beams and girders, and of the resulting bending moments and shearing stresses, including a discussion of the continuous girder. Next follows the subject of resistance to bending and shearing with the introduction of moments of inertia of the usual shapes, the treatment being both analytical and graphical and very completely illustrated by practical examples. In Chapter 19 there is a short presentation of the subject of torsion, and combined bending and torsion, followed by the subheading: "Thrust and Induced Bending," under which heading the Rankine-Gordon formula for columns is analytically deduced. The treatment of this subject of column formulæ, to which most modern writers have devoted much space, is here very brief, being confined to the rational and empirical development of the Rankine-Gordon formula, all others being brushed aside in the following language: "This formula for many years was thought to be too general and in America most eminent engineers made formulæ of their own of like form but varied to suit different cross sections, in a way that led to great confusion. Fidler in the most skilful way arranged the Rankine-Gordon formula in tabulated results which agree with great exactness with the results of more recent exhaustive and elaborate experiments made on struts with the skeleton sections. His tabulated results agree also with the results of the special formulæ for special section."

The authors' criticism of Euler's formula is also worth noting: "In our opinion Euler's formula is quite unsuited for struts for heavy engineering steel work. Euler contemplates a load which will *just not bend* the strut. Now the whole duty of a steel strut in a structure is to resist bending and bend it will no matter how it is designed, for it will take a *set* to one side or other with its own weight if with nothing else; for the weight of the immense struts in modern structures is very considerable. Also heat will distort a strut; and in riveted work the straining of the adjacent members sends bending strains along a strut, which must be designed with an ample radius of gyration, and it is undesirable to talk about a load which will *just not bend* it."

Chapter 20, treating of the steel arched girder or the braced arch, as Americans usually term it, is in the writer's opinion, the most unsatisfactory chapter in the book. The subject is thoroughly discussed in a general way and under all conditions, but there is no analytical treatment of the particular cases, and it is almost inconceivable that a beginner, having read the book conscientiously up to this point should be able to understand from the graphical presentation here given, how to take out the stresses in a braced arch. "For bridges," say the authors, "the steel arched girder seems likely to entirely supersede the suspension bridge." This statement may be true to some extent with English engineers, but American Engineers as a rule are governed in the selection of the braced arch or the suspension bridge by the local conditions and problems which affect the cost and which have to be solved for each case specially and separately. Such a statement as that quoted, therefore, seems wide of the mark.

In Chapter 21, on the other hand, there is a very simple and complete discussion of the analysis of triangular trussing of girders with horizontal chords. The authors claim to have followed the demonstrations of Lévy on this subject, but they have gone further in some instances and the writer has seen no better presentation of this subject in the English language than is here found. The treatment is thoroughly analytical containing rational, not empirical, solutions for the necessary and sufficient weight of a girder. This chapter alone should make the book of great value to the reference library.

The last Chapter, 22, deals with the scientific design of masonry arches and contains graphical as well as analytical solutions of the problems involved, and several tables of practical value. Carefully prepared examples illustrate this part of the work and the pictorial illustrations are particularly instructive and intelligible.

As a whole, this work is much too analytical to become an elementary text book for American students, but possesses great value as a reference work for those wanting a more detailed analysis of some of the subjects than is presented in the ordinary text books. An abstract analysis of the most general case is not as easily comprehended and applied by the beginner as are separate solutions of the most useful particular cases. The graphical demonstrations of many of the problems are somewhat cumbersome and not presented clearly enough for the beginner, but in justice to the authors, it should be said that they disclaim any intention of teaching the subject of graphical statics in this volume. The analytical demonstrations, on the other hand, are for the most part very clear and thorough and their practical application is illustrated by carefully prepared examples.

All of the subject matter of the book has been arranged with careful attention to a rational development, the different theorems and demonstrations being built up step by step consecutively from preceding matter. A discussion of the practical value ot results arrived at seems to have been secondary to the main object of establishing a complete theoretical development of the elementary subject. There is little or no reference to such practical topics as factors of safety, permissible unit stresses, wind forces, details of construction, or shop practice, etc., etc., which are usually given prominence by modern writers on applied mechanics. It is perhaps as well to separate topics relating to strength and quality of materials from a theoretical work on mechanics, although it is not usually done. All things considered it seems that this volume might have been more appropriately called "Theoretical Applied Mechanics" if not an inconsistent title.

W. W. CREHORE.

Astrophysical Problems. By AGNES M. CLERKE. London, A. & C. Black, 1903. Pp. 545.

Miss Clerke's admirable presentation of the past and present of astrophysical knowledge in this book supplies the astrophysicist with a compendium of facts and a body of discussions which will doubtless in many cases serve as the starting points for new discovery. After an introduction, the main divisions are: (1) Problems in Solar Physics, (2) Problems in Sidereal Physics. Fourteen chapters are devoted to minute and particular discussion of the various aspects and problems connected with corona, chromosphere, reversing layer, and photosphere, together with the problems of "the sun's rotation," "the solar cycle," and "the sun as a whole."

In part 2, after an introductory chapter on the progress of sidereal physics, twelve chapters are devoted to the classification of stellar spectra and a discussion of spectral types. The subject of stellar variables is is treated at length in eight chapters, including a chapter on temporary stars. Star clusters are treated in four chapters, and nebulæ in ten. The book closes with a discussion of the physics of the Milky Way. An appendix contains a table of stars with variable spectra, and a list of spectroscopic binaries. The book has been very carefully and fully indexed, and abundant references to the literature appear as footnotes to the text. That the illustrations, which are numerous, are not equal to the text is due to the selection by the publisher of a soft rough-surfaced paper, not well suited to bring out that fineness of detail in the plates which is indispensable in the reproduction of star and spectrum photographs.

The book is more than a compendium or compilation of fact and theory, it is an interpretation of results and a judicial weighing of evidence. Even in parts of the subject where evidence is most chaotic, and the discussion most involved, the exposition is clear and the main points at issue are rarely lost sight of. The work abounds in suggestion and often indicates specifically the directions in which important new facts should be sought. The clear and vivacious style of the author, in which the utmost possibilities of our language are employed to avoid the sin of vain repetitions, makes the presentation of facts, however dry and wearisome in themselves always lively and interesting reading. To the physicist the book will prove a valuable possession, to the astrophysicist it must needs be indispensable. If equal talent could be induced to do for other collateral branches of physics what Miss Clerke has so successfully done for astrophysics, it would mark a most important achievement.

E. F. Nichols.

Elements of Physics. By E. J. Andrews and H. N. Howland. New York, The Macmillan Company, 1903. Pp. i–ix, 1–386 and Manual of Experiments, pp. 52.

In the preface the authors state their aims to be: (1) To readjust the limits of the subject, (2) to give clear notions by means of the scientific method, (3) to make prominent the practical bearings of physics, (4) to base the work on a few fundamental principles. In the main we think they have succeeded. The book is carefully written, parts are well arranged, many parts having been expanded more than is usual. Its size impresses one as large for an elementary book. Part of its bulk is accounted for by the Manual of Experiments comprising 52 pages which has been bound with the text. The book is a text-book for high school pupils' use. It concerns itself with explaining physical phenomena. No experiments for the lecture table or for the student are found in the body of the book. As noted already 63 experiments for students comprise 52 pages at the end of the book. Teachers will always differ as to the kind of experiments which should be introduced into a laboratory. In our opinion experiment 1 on Inertia, experiment 2 on Porosity, experiment 3 on Cohesion, experiment 9 on The Effect of Mass on Falling Bodies, experiment 28 on the Production of Heat, experiment 31 on the Conduction of Heat, and experiment 48 on The Motion of Sonorous Bodies, are all more suitable for the lecture table than for the laboratory. The remainder of the experiments, although suitable enough for laboratory use, are as a rule very easy, much easier than those described in the Laboratory Manual of Timmerman, Cheston and Dean to be described later on.

The authors have tried to make an interesting book and have thus emphasized the phenomenal and experimental as contrasted with the mathematical side of the subject. If the book gains somewhat in interest by this it loses that elegance and precision which one feels in some other books, Carhart and Chute for example.

Some devices introduced are to be commended for originality and clearness. This is true of Fig. 130, which represents a water-analogy of Wheatstone's bridge. No attempt has been made to emphasize the importance of the cuts. They are clear enough but inconspicuous and often crude. The two time-worn diagrams on page 166 which represent in cross-section the parts of a steam-engine and which have done service in so many different books, provoke a smile by their appearance here. They both contain a serious mistake which it is surprising has been allowed to go so long uncorrected.

Writers of elementary text-books in physics are liable to go to one or the other of two extremes. They either make the subject dry and uninteresting by making discussions brief and mathematical, or by avoiding mathematics and introducing much discussion of phenomena and experiments expand the subject to great length. This latter method often leads to prolixity as appears at times to be the case with the book before us. We note the expressions "of course" and "in fact" seven times repeated on six consecutive pages and in every case these expressions might be omitted without in any way obscuring the meaning of the text. Words of this character in a text-book are not only superfluous but a positive blemish.

On page 173 "*artificial* ice" is referred to and the process of its manufacture explained. As the manufacturers of this article are themselves very particular to call it *manufactured* and not *artificial*, and this for obvious reasons, it would seem as though writers of text-books ought to follow the example of the manufacturers. The tendency to prolixity becomes in at least one instance "talk." This appears in the paragraph on "Perpetual Motion," page 175. We note one mistake. On page 151 is this definition: "The heat required to raise any substance one degree will be its specific heat." This is really a definition of *thermal capacity*. The definition above should have inserted after *raise* "one gram of," in which case it becomes correct. The book contains numerous problems and exercises which are an important and very useful feature.

R. H. CORNISH.

Entropy. By JAMES SWINBURNE. Westminster, Archibald Constable & Co., London, 1904. Pp. x + 137.

Some time ago, in an address to the Institution of Electrical Engineers, Mr. Swinburne made a remark upon the definition of entropy and its use by engineers which has been the occasion of a spirited discussion in several engineering journals. The remark was to the effect that no English work upon the steam-engine gives a correct definition of this quantity, and that most treatises on physics, English and foreign, also contain incorrect definitions. The present look is an outcome of this disdussion and sets forth in detail the author's position. It must not be inferred, from the somewhat sweeping statement just quoted, that the book belongs to the class which includes the works of the circle squarers and the anti-Newtonian astronomers. It does not hold that the results of the founders of thermodynamics are wrong, but only that their mode of exposition was unfortunate in that it has led astray many of their followers, including most engineers and text book writers, particularly in the treatment of irreversible processes, that is to say, the only ones which actually occur in practice.

Most of us will be ready to agree with the author as to the errors in many text books, and the desirability of a more careful treatment of irreversible processes. But there is likely to be more difference of opinion in regards to the alternative which he offers. Very radical changes are suggested in definitions, in axioms, and in the interpretation of equations and diagrams; and some of these, at least, are of doubtful utility. Some of the difficulties, which the author finds in the ordinary presentation, have their origin in his unreserved adoption, from the text books which he criticizes, of the concept, "heat of a body," or "quantity of heat in a body"; that this is a fertile source of confusion is not surprising when it is remembered that entropy was introduced by Clausius just because there is no physical reality corresponding to these phrases. Again, the views of the author upon the nature of the entropy-temperature diagram are not likely to meet with universal acceptance. Students of elementary mechanics find difficulty in comprehending the law of action and reaction until they clearly recognize that there are two bodies (or two parts of the same body) concerned, and that the "action" is the force upon one, the "reaction" upon the other. In like manner, the normal difficulties of the study of irreversible thermodynamic processes are greatly exaggerated if one is allowed to forget that, in such a process, there must be two bodies, or at least two parts of the same body in different states with regard to temperature and pressure. Remembering this, it is plain that neither the entropy-temperature nor the volume-pressure diagram is suitable for representing such processes. If parts of a body have different pressures and temperatures, its state cannot be represented upon these diagrams, for no averaging of the "intensities" is permissable; and if a body, homogeneous with respect to temperature and pressure, goes through any process with an outside body, the trace of its series of states upon either of these diagrams can give no indication as to whether the process was performed reversibly or irreversibly. For such purposes, diagrams, in which additive quantities like volume, energy and entropy are the coördinates, are alone suitable; and this was clearly pointed out by Gibbs in the paper in which the entropy-temperature diagram was first described. In plotting the entropy-temperature diagram for the steam-engine, complications of this sort, incident upon wire-drawing, the exchange of heat with the cylinder walls, etc., together with the indefiniteness in the notion of heat referred to above, lead Mr. Swinburne to the conclusion that areas on this diagram are not quantities of heat unless the processes are reversible. An analogous and parallel conclusion would be that areas on the volume-pressure diagram are not quantities of work unless the engine and shafting are frictionless. It is most necessary that the engineer should recognize that the entropy-temperature diagram, as usually constructed, does not give exactly the work done in the cylinder, just as it is necessary for him to make a distinction between indicated and brake horse-power; but a little care in specifying what entropies, temperatures and works one is dealing with, renders unnecessary, it seems to me, a change in the fundamental interpretation of either diagram.

Although the reader may differ with the author upon many points, he cannot fail to be sensible of the service which has been done in calling attention to difficulties and to errors, actual and potential. Much originality and independence of thought is displayed, and there is no special pleading but a very honest endeavor to clear up difficulties and get at the truth. H. A. BUMSTEAD.

Electrical Machinery. Vol. I., Electric, Magnetic and Electrostatic Circuits. By HARRIS J. RYAN, HENRY A. NORRIS and GEORGE L. HOXIE. New York, John Wiley & Sons, 1903. Pp. 246.

There are to be two volumes to this work on Electrical Machinery, in which both direct and alternating currents and machines are to be treated. Volume I. covers the laws of the electric, magnetic, and electrostatic circuit, and is intended as an introduction to Volume II., in which the construction and performance of electrical machinery is to be discussed.

The material of Volume I. is stated to be the result of several years of experience in the class room at Cornell University. The plan of the book is to found the treatment of the subject upon the laws of alternating currents and to consider continuous current phenomena as special simplified cases of these. While this is scientifically the most general plan it would seem to make the understanding of continuous current phenomena unnecessarily difficult for the student. The authors state, however, that they have found that this plan maintains the interest of the student and economizes his time, and that it has given very satisfactory results at Cornell.

The first volume is divided into ten chapters with the following headings: "Electricity and Magnetism," "Periodic Curves," "Complex Quantities," "Laws of the Electric Circuit," "Electric Power," "Magneto Motive Force," and the "Laws of the Magnetic Circuit," "Rotating Magnetic Fields," "The Electrostatic Field," "Losses in Electric Circuits." In the first two chapters the elementary principles and units of electricity and magnetism are briefly given; these are illustrated with a number of problems and with clear diagrams. Periodic curves are taken up at length by graphical and analytical methods. Fourier's theorem and a method for the general analysis of any periodic curve are given in detail, and the application of the method is shown by a number of examples illustrated with exceptionally clear diagrams many of which occupy a full page. In the chapter on complex quantities this analytical method for expressing vectors is explained and the algebraic operations with complex quantities are given. These are made use of in the next chapter for solving series and parallel circuits with resistance, inductance and capacity. Graphical methods are only given for a few simple series circuits, but not for parallel circuits.

Electric power calculations in alternating current circuits are discussed in Chapter VI.; the errors involved when equivalent sine waves are used for irregular waves are carefully pointed out. A power problem in irregular wave forms is given in detail, the correct power being calculated by means of harmonic component E. I. products.

The chapter on electrostatic field is unique and full of valuable material, much of which represents the researches of Prof. Ryan. The existence of an electrostatic flux circuit is shown and an attempt is made to compare it with the magnetic flux circuit. The phenomenon of corona is discussed in detail and a number of experiments are described to illustrate corona effects. The authors point out that insulators for high potentials must be so proportioned that the dielectric flux set up through them will not be sufficient to cause corona, because this would be highly destructive and would also represent a considerable waste of power. The necessity for avoiding corona formation in dielectric strength testing is also explained, and the precautions which must be taken to avoid this are stated. In the appendix a short discussion is given of the limiting voltages for transmission lines. A table giving the minimum diameters of wires to avoid corona for voltages from 50,000 to 250,000 when the distance between the wires is 48 inches is given. In the last chapter on losses in electric circuits mathematical discussions of the various losses are given and a number of formulæ are deduced. Some experiments on a high potential transmission line made by Mershon are described and the results of these tests are compared with those obtained from the mathematical laws.

It may be safely said that this book is unique among electrical books, and that it forms a valuable addition to electrical literature. It is written throughout in exact and concise language and is illustrated with many clear and carefully executed cuts. Over seventy problems are given, many of which are completely solved in the text. This is a valuable feature for the student.

While the book is primarily intended for technical schools, for which purpose it is admirably adapted, it will also prove most valuable to the practicing electrical engineer. It is to be hoped that its companion volume will soon make its appearnce. A. F. Ganz.

Secondary Batteries, their Theory, Construction and Use. By E. J. Wade. The Electrician Printing Co., London; D. Van Nostrand & Co., New York, 1903. Pp. ix + 492.

This volume may be conveniently divided into four portions. The first contains a very complete description of the various forms of storage battery introduced since 1881 and a brief chapter on secondary cells in which other substances than lead are employed. A second part deals with the properties and behavior of lead cells with numerous diagrams giving the characteristic curves for the performance of secondary batteries under varying conditions of charge and discharge, one chapter is devoted to the chemistry of the lead cell. This portion of Mr. Wade's book is followed by a series of chapters dealing with the design, manufacture, treatment, testing, erection and regulation of storage batteries. These chapters containing as they do numerous facts of practical value based upon actual experience are of especial value to those engaged in the installation and management of batteries.

The volume closes with a chapter entitled "Present day cells" in which those forms which have established themselves in England and the United States are considered in greater detail. The prevailing forms in use on the continent of Europe are likewise noticed but more briefly.

E. L. N.

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VOLUME XVIII NUMBER 6

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY
EDWARD L. NICHOLS
ERNEST MERRITT, and FREDERICK BEDELL

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JUNE, 1904

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THE

PHYSICAL REVIEW.

THE REFLECTING POWER OF SELENIUM AS DETERMINED BY A SPECTROPHOTOMETER.

By C. K. Edmunds.

THE present photometric measurements of the reflecting power of selenium are confined to the visible region of the spectrum, and are divided into two main parts. (1) Determination of the reflecting power of selenium for several different wave-lengths for normal incidence. (2) Determination of the reflecting power for three different wave-lengths of light polarized in and normal to the plane of incidence, for a range of incidences from 20°–80°. The results under (1) are compared with the reflection curve secured by calculation from the dispersion and absorption curves; those under (2) are compared with the values calculated by means of Cauchy's formulæ, assuming the values of the absorption coefficient and refractive index secured from the metallic reflection experiments.

Apparatus and Method of Observation.

The spectro-photometer used was made by Schmidt and Haensch after Professor Brace's[1] design. It consists essentially (Figs. 1 and 2) of a double prism P with a narrow silvered strip SS on the face AD of the right half. Light of the same wave-length is thus brought by direct transmission from the collimator T, and after reflection at the silver strip from T', to the same focus in the observing telescope R. When the eyepiece is removed and the prism viewed through a slit in the focal plane of R, the eye sees three fields (Fig. 3), the central one *ABCD* illuminated by light from the right collimator T', and the upper and lower ones *ACF* and *BDG*, by light from the left collimator T. The fields meet in the sharp edge of the silver strip. A match in intensity is secured by altering the width of T' which must be bilateral in order that the spectra from the two collimators may be kept in-step, after being once adjusted, as the slit T' is changed in width. The condition of photometric equality is determined by the vanishing of the line of separation between the two portions of the field of view illuminated respectively by the direct and the reflected light. By shifting the telescope R, different portions of the spectrum may be brought into the field of view and so the intensities of the various colors of the reflected beam may be compared with the corresponding colors of the direct light, and the reflecting power for any desired wave-length determined.

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[1] Brace, Phil. Mag., 48, 420–430, 1899, and Astro. Phys. Jour., 11, 6–24, 1900.

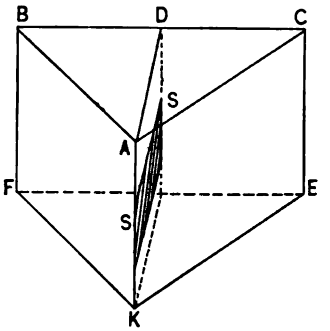

Fig. 1.
Double Prism, Silver Strip: *ss*.

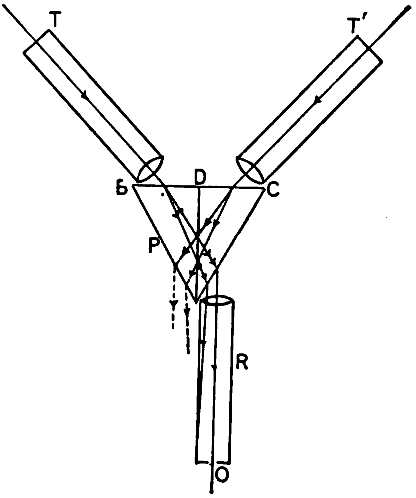

Fig. 2.
Optical System.

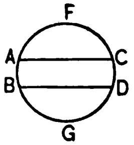

Fig. 3.
Field of View.

The conditions of an ideal photometer screen as given by Lummer and Brodhun[1] are met by this instrument in a manner described by Tuckerman,[2] who has so fully explained the adjustments necessary to their fulfillment that no additional account need be given here.

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[1] Lummer and Brodhun, Zeitschrift für Instrumentenkunde, 12, 137–138, 1892.

[2] Tuckerman, Astro. Phys. Jour., 147, 149, Oct., 1902.

GENERAL METHOD OF OBSERVATION.

The slit of one collimator T is, after the initial adjustments of the photometer, kept fixed in width throughout a whole series of comparisons. The slit on the other collimator T' is controlled by an accurately turned screw by means of which its width can be altered at will by a known amount, and thus the total amount of light passing down this collimator can be changed as desired. The amount of light coming down the collimator with the fixed slit can be changed without altering the width of the slit by means of a rotating disk mounted so as to rotate directly in front of the fixed slit and to cut off the light during a certain fraction of each revolution. The reflecting power of the given mirror is determined in the following manner. Light from the same source or two sources practically identical, is in part sent down the collimator with the fixed slit and in part sent down the collimator with the adjustable slit the width of which is altered till a photometric equality of the two beams is secured in the field of view. Call the width of the adjustable slit under these conditions S'.

The mirror to be investigated is now introduced in the path of the light on the way to the adjustable slit and the direction of the incident beam and the portion of the mirror altered till after reflection at the desired incidence the light again enters the adjustable slit and so into the photometric system. Photometric equality will no longer exist in the field of view, since the reflected beam has been weakened in intensity by the reflection, and a match can be secured by widening the adjustable slit. Call its new width S. Now if the direct ratio-law held (*i. e.*, if the total amount of light passing throught a slit were directly proportional to the slit width) the ratio of the intensity of the reflected light to that of the incident light, *i. e.*, the reflecting power of the mirror for the color matched and for the angle of incidence used would be S'/S, the intensity of a beam being inversely proportional to the width of the slit required to secure a match between it and a fixed illumination.

As a matter of fact, this direct ratio-law does not hold in general and the optical value of different slit widths must be determined for different colors and different intensities of radiation in a manner described[1] elsewhere by Capps and others. By means of calibration curves secured in the manner there described, this ratio-by-slit, *i. e.*, S'/S can be reduced to give the correct value of the reflecting power.

If the reflected light is very much weaker than the direct, the change in width of the adjustable slit required for a match may be too great either for the limited range of the adjusting screw or for employing the best portion of the calibration curve. In this case the amount of light coming down the collimator with the fixed slit may be decreased without altering the slit width, by cutting down the light falling on it by means of a rotating sector of known and adjustable angular value revolving directly in front of the fixed slit in such a way as to cut off the light during a certain fraction of each revolution. The speed at which this sector is run does not enter except that it must be high enough not to cause any flickering in the field of view.

If now, the mirror being removed and the sector at rest so as to allow full illumination of both the fixed and adjustable slits, the width of the latter required for a match be S', the mirror is put in position, the reflected beam sent upon the adjustable slit, the rotating sector made to revolve and its angle changed till a match is again nearly secured in the field of view. An exact match can now be obtained by a slight change in the width of the adjustable slit. As before call its new width S. If the angle of the sector used was such as to allow light to pass during $1/n$th of a revolution, then the reflecting power is $S'/S \cdot 1/n$. If the change in the width of the adjustable slit is not small, then the value of S'/S must first be optically calibrated by means of the curves showing the variations from the direct ratio-law, and then the reduction factor $1/n$ applied to give the final value of the reflection power for the color matched and the angle of incidence used.

CALIBRATION OF SPECTROPHOTOMETER.

Owing to the curvature of the luminosity-curve of the radiant the illumination is not in general proportional to the slit width. With a bilateral slit the direct ratio holds at points where the curve is a straight line, but where the liminosity-curve is convex to the axis of wave-lengths, the intensity of the light passing down the collimator *T'* for different widths of slit increases in a greater ratio than the width of the slit, the reverse being true for the concave portions. Hence the discrepancies, which are greater the greater the width of the fixed slit *T*, are in an opposite sense in the yellow from those in the red and blue; slit readings give too high a ratio for red and blue light, too low for yellow.

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[1] Murphy, Astro. Phys Jour., 6, 1–10, 1897.
Brace, Phil. Mag., 48, p. 425, 1899.
Capps, Astro. Phys. Jour, 11, 25–35, 1900.

In the present experiments the bilateral slit *T'* was calibrated optically by means of a rotating sector, for the width of *T* (.3 mm. in most cases) and the various wave-lengths used, in the manner devised by Professor Brace and employed by Capps and others. A simple cardboard disk mounted on a small motor, with its circumference divided into a number of parts and slotted out to different depths between different radii as shown in Fig. 4, was rotated between the source and the slit *T*, so that the different sectors covered the slit in its successive positions, and thus the intensity of the light coming down the collimator *T* was varied in known ratios depending on the angle of the sector used. A twelve part disk was used, with a greatest diameter of 24 cm. Since Capps[1] has recently fully described the method and results of similar calibrations further detail will not be given here, other than to point out that the final readings were made by a combined use of the variable slit and the rotating sector. Approximate matches were secured by cutting down the light entering *T* by appropriate sectors of known angular value and only the final adjustment for a match was made by varying the width of slit *T'*, the effort being to confine the readings to as nearly the same region on the screw operating *T'* as possible. Whenever the variation was sufficiently great the ratio by slit readings was corrected by means of the calibration curves and the reduction factor of the disk applied to this corrected ratio. This was the method first used by Brace and More[2] in 1899, it eliminates to a great extent any errors of the screw, giving greater accuracy in the optical evaluation of the slit comparisons.

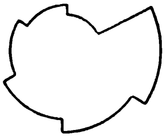

Fig. 4.
Calibratory Disk.

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[1] Capps, Astro. Phys. Jour., 11, 25–35, 1900.

[2] Brace, Bull. Am. Phys. Soc., 1, 2, pp. 29–31; also Brodhun, Zeitschrift für Instrumentenkunde, 20, 210-212, 1900.

With narrow slit width, such as here used, the zero correction for T' becomes an important factor. From time to time between various sets of observations the bilateral slit T' was subjected to a special test, and by means of a micrometer microscope its width for different readings of the screw's divided head were noted in the region of small slit widths, and from them the true zero was determined by extrapolation. After starting to use the slit, it was never again closed without the zero being redetermined. Final settings for photometric equality were always made with increasing slit-width.

Auxiliary Reflecting Spectrometer.

The general arrangement of the apparatus is shown in Fig 5. S is the Brace's spectrophotometer. S' is the auxiliary reflecting spectrometer carrying the mirror M mounted on the graduated table V in the center of the larger table D, about which the collimator T'' can be rotated for any desired angle of incidence. L and L' are the 110-volt Nernst filaments enclosed in the boxes B and B'. g is a window of thin milk glass, and g' is a screen of fine ground glass. N is a Nicol's prism of 3 cm. aperture, by means of which

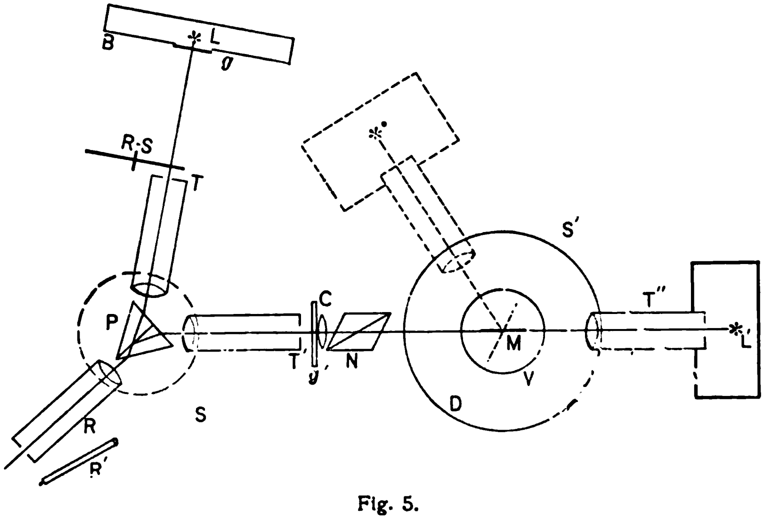

Fig. 5.

Assembly of Photometric Apparatus. Dimensions: From center of P to T, or to T', approximately, 30 cm. Diameter $V=13$ cm., diam. $D=40$ cm., from T to $g=40$ cm. Focal length of T'', approx., 35 cms., aperature 4 cm. in diam. From center of P to M, approx., 80 cm.

the reflected light can be polarized in any desired azimuth, the zero position of the Nicol being determined in a way described presently. C is a condensing lens which focuses the reflected light on the bilateral slit T'. $R-S$ is the rotating divided disk mounted on a motor carried by a lathe tool-carriage so as to shift the disk in its own plane back and forth before T.

The radiant L was mounted on an extension rigidly connected with the platform carrying the spectrophotometer S. The motor carrying the rotating sector was mounted on a heavy stone sill entirely separate from the other mountings so as to cause no vibration. The ground glass g', the lens C and the Nicol N were all mounted on the base of S. The rådiant L' was rigidly attached to the collimator arm of T''. The various dimensions were as shown in the diagram, approximately.

Light from L passed through the milk glass g, was then interrupted by the rotating sector $R-S$ entered through the slit T, was rendered parallel by this collimator, suffered refraction and dispersion in P and entered the telescope R where it was viewed through the ocular slit O. The slit T was kept at a fixed width and the intensity of the field from T altered by shifting the sector $R-S$.

Light from L' was rendered parallel by the collimator T'', fell on the mirror M at any desired incidence, (the value of which was given by the circle reading on V, which was graduated to 1′) and after reflection was polarized in any desired azimuth by passing through N, was focused by C on the bilateral slit T' after passage through the ground glass screen g', which helped to give a uniform field, was again rendered parallel by the collimator T' and suffered refraction, reflection and dispersion in P, the part striking the silver strip SS (Fig. 1) entering the viewing telescope R and forming the central part of the field as viewed through the ocular slit O. The part of the light from T' which passed above and below the silver strip SS was refracted out and lost in the box surrounding P. The intensity of this central portion of the field was changed by altering the width of T' by means of a micrometer screw the setting of which could be read off by means of a small auxiliary telescope R' mounted along side of R.

The smallest angle of incidence at which observations could be secured was 7°, and the values recorded for normal incidence are really for $\varphi = 7° \pm$. It is not thought necessary, however, to make any allowance for this small angle.

In the following tables the recorded values for slit width of T' are the means of ten settings in each case. The variation in such a set of ten readings is exhibited by the sample given in Table I. The maximum deviation from the mean is 1.5 per cent. and the probable error of the mean value is .4 per cent. The probable error in the final values of the reflection power is about .75 per cent., though it is very likely greater than this for the extreme blue, on account of the difficulty of good seeing in that region.

COMPARISON OF THE VALUES OF THE REFLECTING POWER AS SECURED BY DIFFERENT METHODS.

There are in general two ways of determining the reflecting power of a given substance, (1) direct and (2) indirect. (1) The direct method is by such photometric measurements as have just been described. (2) The indirect method involves the use of the formula

$$R = \frac{(n-1)^2 + k'^2}{(n+1)^2 + k'^2}, \qquad (a)^1$$

where

n = refractive index

and

k' = absorption coefficient,

at normal incidence, for the wave-length considered.

These optical constants n and k' can be determined either (*a*) directly by measurements with prisms and thin films or (*b*) indirectly by calculation from the constants of elliptical polarization as described in an earlier paper.

The values of the reflecting power for both old and new mirror are, together with those secured from the experiments of others presented in Table III., the first column of which gives the wave-length of the incident light, the second the reflecting power as I have calculated it from Pfund's observations (see page 395) of the absorption and refraction indices by means of equation (*a*). Column 3 gives the values of the reflecting power as calculated by the same

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[1] Cauchy, Compt. rend., T. VIII., 1839, p. 560.

OBSERVATIONS.

TABLE I.

Vitreous Selenium. Mirror 5 months old. Direct light. Date: March 25, 1903.

Telescope.	5.58.	6.08.	6.33.	6.83.	7.08.	7.58.	7.83.
Wave-length.	489 $\mu\mu$.	524.	545.	589.	622.	701.	748 $\mu\mu$.
	Divs						
Slit	124	128	136	129	147	190	212
	3	24	5	30	44	85	2
	3	27	3	30	43	91	4
	3	27	8	29	43	92	4
	2	29	5	29	43	88	2
	3	26	8	31	43	89	2
	2	24	5	32	47	89	3
	3	27	6	28	47	90	2
	4	26	7	31	43	87	4
	123	128	5	132	145	189	213
Means	123.0	125.6	135.8	130.1	144.5	189.0	212.8
Zero correc.	−19.8	−19.8	−19.8	−19.8	−19.8	−19.8	−19.8
Corrected mean	103.2	105.8	116.0	110.3	124.7	169.2	193.0
Maximum deviation	.1	2.4	2.8	2.1	2.5	3.0	1.2
Or	1 %					1.5 %	
Probable error in mean	.04					.4	
Or	.04%					.4 %	

REFLECTING POWER OF A MIRROR OF VITREOUS SELENIUM.

TABLE II.

Normal Incidence.

Surface 5 months old.

Wave-length.	489 $\mu\mu$	524	545	589	622	701	748 $\mu\mu$
			Corrected Slit Readings.				
Reflected : S	143.35	125.60	167.25	174.65	159.91	148.41	144.4
Direct : S'	103.2	105.8	116.0	110.3	124.7	169.2	193.0
Reduction factor of disk : $1/n$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{6}$
$S' \cdot 1/n$	34.4	35.266	38.66	36.766	41.566	28.2	32.166
R in %	24.01	28.08	23.12	21.05	25.99	19.00	22.28

Fresh Mirror (i. e., a day or two old).

Wave-length.	432 $\mu\mu$	454	489	524	589	622	660	748 $\mu\mu$
S	207.2	245.6	274.4	265.6	281.7	287.2	307.1	432.4
S'	192.0	197.9	204.0	209.3	218.0	746.5	334.4	381.5
$1/n$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{9}$	$\frac{1}{4}$	$\frac{1}{4}$
$S' \cdot 1/n$	64.0	65.97	68.0	69.77	72.67	82.17	83.6	95.38
R in %	30.89	26.86	24.78	26.27	25.80	28.61	27.22	22.06

formula from the values of the optical constants deduced from the metallic reflection experiments of various observers by application of Walter's formulæ.

TABLE III.

Reflecting Power of Vitreous Selenium.

1	2 Calculated from Pfund's Observations.	3 Calculated from Metallic Reflection Experiments.	4 Directly Observed by Nutting.	5 Directly Observed by Edmunds.	
214			.0998	New (*a*)	Old (*b*)
280		.2008			
334			.1265		
395			.1584		
400	.2703				
410			.1667		
415	.2713				
425	.2687				
431		.2679	.1583		
432		.2710		.3089	
439		.2534			
442	.2692				
454				.2686	
466	.2724				
486		.2723			
489				.2478	.2401
490	.2745				
508		.2590			
510			.1685		
515	.2662				
524				.2627	.2808
527		.2706			
545					.2312
550	.2555	Quincke	.1801		
589	.2417	(.2722) .2600	.1834	.2580	.2105
605			.1763		
620			.1434		
622				.2861	25.99
631		.2174			
640	.2202		.2194		
656		.2609			
660				.2722	
701					19.00
710	.2052				
721		.2101			
735		.2279			
748				.2206	22.28
760	.1989				

Column 4 presents Nutting's[1] photometrically determined value of the reflecting power, *R*.

In column 5 are recorded my photometric values of *R* for both old (*b*) and new (*a*) mirror.

These results are represented graphically in Fig. 6.

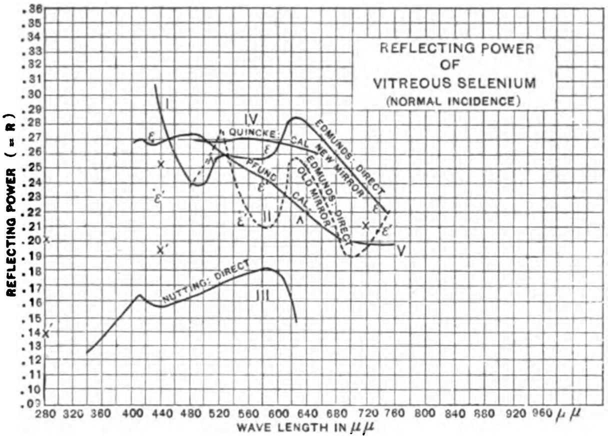

Fig. 6.

Reflecting Power of Vitreous Selenium.

Curve I., photometrically observed for a fresh mirror by Edmunds; II., photometrically observed for a mirror five months old by Edmunds; III., photometrically observed by Nutting, probably for an old mirror; IV., calculated (Edmunds) from Quincke's observation on metallic reflection; V., calculated (Edmunds) from Pfund's direct observations on refraction and absorption. Iso'ated points have been calculated from metallic reflection experiments of various observers, as follows: Edmunds, new mirror ε; Edmunds, old mirror, ε'; Cornu, new mirror x, old mirror x'; Glan, Λ.

THE SURFACE COLOR OF SELENIUM.

The directly determined reflection curve for selenium at normal incidence (see Fig. 6) shows a maximum at about 620 and a minimum at about 490 $\mu\mu$ after which there is a steady rise in the reflecting power as the wave-length is decreased.

The high values of the absorption in the ultra-violet as found by Pfund suggest possible selective reflection in this region. But, as already noted, several attempts to detect "Reststrahlen" in the ultra-violet by successive multiple reflections from six mirrors of vitreous selenium failed to show any selective reflection; in fact, they indicated a slight falling off in reflecting power. This agrees with the drop in Nutting's photometrically observed reflection curve, which occurs at about $\lambda = 410 \mu\mu$ from which point on (*i. e.*, for decreasing wave-lengths) there is a rapid falling off in reflecting power (see Fig. 6).

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[1] Nutting, Phys. Zeit., 201–206, Jan. 1, 1903.

The method followed in looking for selective reflection in the ultra-violet was to allow the light from a cadmium spark to suffer six-fold-reflection at nearly normal incidence from six good mirror surfaces of vitreous selenium, and after the sixth reflection to fall on the slit of a quartz spectrograph in which the light was received upon a photographic plate and an exposure made for a certain known time-interval. Several exposures of different intervals were made on the same plate. The mirrors were then removed and the light from the spark allowed to fall directly on the slit of the quartz spectrograph. Several exposures of different time intervals were again made on the same plate used for the reflected light. Comparisons of the relative density of the developed plate for different wave-lengths showed no decided increase in the reflecting power for wave-lengths from 345 to $229 \mu\mu$.

The relation of reflection and absorption is well illustrated by the curves for selenium. Metallic reflection experiments show a slight maximum in the absorption at about $590 \mu\mu$ and then a steady rise for shorter wave-lengths. The photometrically determined reflection curves show a maximum in reflecting power at about $620 \mu\mu$ and $420 \mu\mu$ which in each case lie on the side of larger wave-lengths from the maxima in the absorption curve, that is, the maximum of the reflection curve is shifted in the direction of the longer wave-lengths with respect to the absorption maximum, while the minimum of the reflection curve lies on the blue side of the absorption-band, a result in full accord with the deductions from formula (*a*).

REFLECTING POWER OF VITREOUS SELENIUM FOR LIGHT POLARIZED IN AND NORMAL TO THE PLANE OF INCIDENCE, AT DIFFERENT INCIDENCES AND FOR DIFFERENT COLORS.

By means of the arrangement of apparatus as pictured in Fig. 5, the light could be received by the selenium mirror M at any desired angle and after reflection could be polarized in any desired azimuth by means of the Nicol *N*, the zero position of which was determined thus:

The polarizing angle of a flint glass prism for sodium light was calculated from $\tan \varphi_p = n$, and $n_D = 1.5183$. The prism was mounted on *V* in place of the mirror *M* and sodium light reflected from one of its surfaces at this polarizing angle 56° 38′. *N* was then turned in its mounting until the light reaching *T′* was a minimum. In this position the polarizing plane of the Nicol was normal to the plane of incidence, and light passing through it was polarized normal to the plane of incidence.

The observations of the reflecting power for light polarized normal to the plane of incidence and for light polarized in the plane of incidence for incidences of 20°, 40° are reproduced as examples, and the final summary (*R* and *R′*) compares the observed values of *R* for incidences 20°–80° with the values computed from the determinations of the refractive index and absorption coefficient previously recounted.

In Tables *R* and *R′* the columns headed *d* give the difference between the observed and calculated values of the reflecting power ($d \equiv$ calculated — observed).

The agreement between observed and calculated values is on the whole fair, being somewhat closer in the case of light polarized in the plane of incidence than for light polarized normally. In the first case the discrepancy is much greater for the larger angles of incidence, probably on account of the greater influence of the surface film at such incidences. In the second case, *i. e.*, of light polarized normal to the plane of incidence, the discrepancy between observed and calculated reflecting powers is greater for the small incidences.

For blue light the values calculated from Pfund's direct measures of refraction and absorption agree very well with the observed reflecting power for light polarized in the incidence plane; though for light polarized normally the agreement is not so good.

For yellow light the values calculated from my metallic reflection experiments agree very well (better than those calculated from other data) with the directly observed values of the reflecting power; though as in all other cases also the highest angles of incidence must be excepted.

No calculated values are recorded for the red ($\lambda = 690\ \mu\mu$) because no sufficiently reliable determinations of the refractive index and absorption coefficient have been made for wave-lengths very near

Reflected Light Polarised in the Plane of Incidence.

		$\phi = 20°$.	
Telescope	7°.50	6°.83	5°.75
$\lambda =$	690 $\mu\mu$	589	501
Disk	.2500	.2500	.3333
S	175.2	172.7	218.4
S'	172.0	175.7	187.1
S'/S	.9875	1.0174	.8567
Calibrated	.9875	1.0174	.8020
Reduced R_i^p	.2469	.2544	.2673
		$\phi = 40°$.	
Disk	.4167	.4167	.5833
S	158.0	149.7	196.0
S'	141.0	126.7	140.3
S'/S	.8924	.8464	.7158
Calibrated	.853	.821	658
Reduced R_i^p	.3554	.3421	.3838

REFLECTING POWER OF VITREOUS SELENIUM AT DIFFERENT ANGLES OF INCIDENCE.

Reflected Light Polarised Normal to the Plane of Incidence.

		$\phi = 20°$.	
Telescope at	7°.50	6°.83	5°.75
$\lambda =$	690 $\mu\mu$	589	501
Reflected: Disk	5/12	5/12 (.4167)	6/12
Slit: S	139.3	120.6	126.5
Direct: S'	68.2	72.0	58.3
S'/S	.4896	.5970	.4609
Calibrated	.466	.631	.420
R_i^s in per cent. reduced	19.42	26.29	21.00
		$\phi = 40°$.	
Disk	5/12	6/12 (.5000)	6/12
S	170.7	166.3	137.3
S'	68.2	72.0	58.3
S'/S	.3995	.2851	.4246
Calibrated	.346	.280	.382
R_i^s in per cent. reduced	14.42	14.00	19.10

TABLE R′.

Reflecting Power, Observed and Computed. Light Polarized in the Incidence Plane.

	λ = 501 μμ					λ = 589 μμ									λ = 690 μμ
		1	2				1	2	3	4					
φ	Observed.	Cal.	Cal.	δ_1	δ_2	Observed.	Cal.	Cal.	Cal.	Cal.	δ_1	δ_2	δ_3	δ_4	Observed.
20°	.2673	.2752	.2914	+.0079	+.0241	.2544	.2813	.2554	.2624	.2764	+.0269	+.0010	+.0080	+.0220	.2469
40	.3838	.3534	.3880	−.0304	+.0042	.3421	.3543	.3278	.3337	.3491	+.0122	−.0143	−.0084	+.0070	.3554
60	.5000	.5055	.5156	+.0055	+.0156	.4871	.5064	.4822	.4864	.5016	+.0193	−.0049	.0007	+.0145	.4670
70	.6583	.6267	.6349	−.0316	−.0082	.6030	.6275	.6068	.6099	.6233	+.0245	+.0038	+.0069	+.0203	.6237
80	.7175	.7886	.7936	+.0711	+.0050	.7185	.7890	.7759	.7776	.7863	+.0705	+.0574	+.0591	+.0678	.7010

$\delta \equiv$ cal. — observed.

For $\lambda = 501\ \mu\mu$, col. 1 has been calculated from Glan's values of $\bar{\phi}$ and $\bar{\psi}$ for λ. $508\ \mu\mu$ which give $n_0 = 2.884$, $k'_0 = .9033$.
" " " 2 " " " " Pfund's values of $n_0 = 3.11$, $k'_0 = .388$ for $\lambda = 501$.

For $\lambda = 589\ \mu\mu$, col. 1 has been calculated from Edmunds' values of $\bar{\phi}$ and $\bar{\psi}$ for *new* mirror, giving $n_{\bar{\phi}} = 2.8198$, $k'_{\bar{\phi}} = 0.8073$.
" " " 4 " " " " the same reduced to give $n_0 = 2.8076$, $k'_0 = .7637$.
" " " 2 " " " " Edmunds' values of $\bar{\phi}$ and $\bar{\psi}$ for *old* mirror, giving $n_0 = 2.406$, $k_0' = 0.9863$.
" " " 3 " " " " Wood's values of $n_0 = 2.925$, $k_0' = 0.155$.

TABLE R.

Reflecting Power, Observed and Computed. Light Polarized Normal to the Incidence Plane.

ϕ	$\lambda = 501\ \mu\mu$					$\lambda = 589\ \mu\mu$									$\lambda = 690$
		1	2				1	2	3	4					
	Observed.	Cal.	Cal.	δ_1	δ_2	Observed.	Cal.	Cal.	Cal.	Cal.	δ_1	δ_2	δ_3	δ_4	Observed.
20°	.2100	.2336	.2486	+.0236	+.0386	.2629	.2387	.1963	.2209	.2341	−.0242	−.0666	−.0429	−.0287	.1942
40	.1910	.1710	.1957	−.0200	+.0047	.1400	.1716	.1501	.1556	.1675	+.0316	+.0101	+.0156	+.0275	.1442
60	.0635	.0575	.0605	−.0140	−.0030	.0697	.0592	.0531	.0448	.0563	−.0105	−.0166	−.0249	−.0134	.0438
70	.0362	.0125	.0065	−.0237	−.0297	.0314	.0162	.0305	.0013	.0146	−.0152	−.0009	−.0301	−.0168	.0199
80	.1187	.0991	.0772	−.0196	−.0415	.1000	.1069	.1544	.0898	.1071	+.0069	+.0544	−.0102	+.0071	.0842

The calculated values are based on the same determinations of n_0 and k'_0 which are used for Table R′, just given. (δ = cal. − observed.)

this. The calculations are somewhat tedious and were not thought justified if based on interpolated values of the optical constants.

The curves in Fig. 7 showing the reflecting power of selenium at various incidences and for the three colors, $\lambda = 501\ \mu\mu$, $589\ \mu\mu$ and $690\ \mu\mu$, indicate that at 70 degrees incidence there would be very little reflected light of any color polarized normal to the plane of incidence, while in the reflected light polarized in the plane of incidence there would be an excess of blue and red, and a minimum of yellow. This is an agreement with some previous observations made to detect any trace of surface color in the visible region of the spectrum. Ordinary light was reflected from vitreous selenium and the reflected light viewed through a Nicol's prism. The angle of incidence was changed and the azimuth of the Nicol step by step, and it was found that at about 70° incidence, reflected light polarized in the plane of incidence showed a marked blue tint.

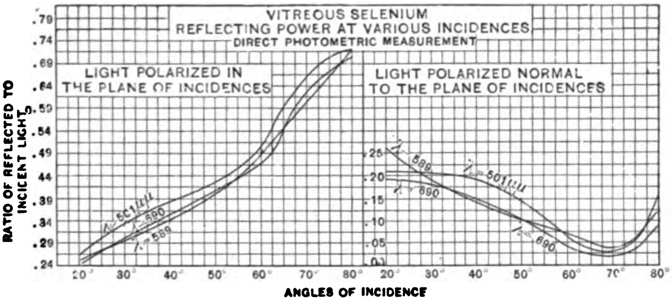

Fig. 7.

Murphy has given results for the intensities of polarized light reflected from the face of a Steinheil prism as determined by means of a Lummer-Brodhun spectral photometer. They show a close agreement between the observed and computed values, the differences being in every case but a small part of the total incident light. The greatest discrepancy exists for light polarized perpendicular to the plane of incidence, and for the small angles of incidence. The agreement between calculated and observed values of the reflecting power is nearly as good for selenium as it is for glass, especially if we take into account the great difficulty of controlling the surface condition of a selenium mirror as compared with a glass surface.

SYNOPSIS OF RESULTS.

The present photometric measurements of the reflecting power of selenium have shown that there is in general an increase in the reflecting power as the wave-length of the incident light is decreased, there being in the course of this general rise a maximum at about 620 $\mu\mu$ and a minimum at about 590 $\mu\mu$ after which for shorter wave lengths there is a steady increase in reflecting power.

An apparent effect due to lapse of time, *i. e.*, ageing of the mirror in such a way as to form an effective surface layer, greatly modifies this curve. The reflecting power for all wave-lengths is decreased except in the region of 525 $\mu\mu$ where an increase was noted.

Nutting's observed values of the reflecting power are entirely below the field of other determinations and the present experiments would seem to indicate that his mirror had been made some time before using or at least had acquired a surface film similar to that on the mirror described as "old" in this paper.

The relation of reflection to refraction and absorption was treated briefly and the deductions from the reflection formula found to be verified in a general way.

Photometric measures verified Cauchy's formulæ giving the reflecting power of a metal (*i. e.*, a heavily absorbing medium) in terms of the optical constants for various angles of incidence. The agreement between observed and calculated values was nearly as satisfactory as for glass to which Fresnel's formulæ giving the reflecting power of a transparent substance in terms of the refractive index had been applied.

In conclusion, I desire to express my appreciation of the kindness of Professor Ames and of Professor Wood. The latter suggested the investigation to me, and both have given advice and liberal aid throughout the course of work.

PHYSICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
May, 1903.

STUDIES IN LUMINESCENCE. II.

By Edward L. Nichols and Ernest Merritt.

A Spectro-photometric Study of Fluorescent Solutions Belonging to Lommel's First Class.[1]

THE law expressed by Stokes[2] in his memoir entitled "The change of Refrangibility of Light" to the effect that in fluorescence the fluorescent light is always of greater wave-length than the exciting light has been called in question by Lommel, who pointed out that for certain fluorescent bodies there is an unmistakable overlapping of the regions in the spectrum occupied by the exciting light and by the fluorescence which it produces. Lommel made the further very important statement that for this class of substances the character and composition of the fluorescence spectrum is independent of the wave-length of the exciting light. Lommel's results in so far as they had to do with the non-validity of Stokes's law were confirmed by Hagenbach.[3] A few years later Lubarsch[4] published measurements in confirmation of Stokes's law. A later paper by Lommel,[5] in which he described the fluorescence of the so-called chameleon colors, led Hagenbach to new experiments, in the course of which he discovered what he believed to be a source of error in his former measurements, and he reaffirmed the law of Stokes for all such substances. In 1877 Brauner[6] obtained results in confirmation of Lommel's view. In 1879, Lubarsch[7] published further experiments on fluorescence, this time in favor of Lommel's results. Lamansky[8] in 1879 described measurements in confirmation of Stokes's law. In a still later paper Hagenbach[1] returned to the defence of Stokes's law as against Lommel[2] and Lubarsch,[3] who in the meantime had published further articles dealing with his objections and criticizing Lamansky's method. Wesendonck[4] in 1885 made observations with the sun's spectrum, using two concave mirrors and a prism, in the course of which he obtained very conclusive evidence that the fluorescence of naphthalin-roth extended to wave-lengths shorter than that of the exciting light. In 1886, Stenger[5] took the question up at length. He found that whether he used Hagenbach's method of illuminating the free surface, Lommel's method of grazing incidence through the side of a flask, or Lubarsch's fluorescent eye-piece, his measurements confirmed Lommel as to the invalidity of Stokes's law but not as to the independence of the fluorescent spectrum from the character of the exciting light. He also made experiments in colaboration with Hagenbach, who was finally converted to the same view.

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[1] Read at the St. Louis meeting of American Physical Society, Dec. 29, 1903, under the title "The Spectrometric Study of Fluorescence."

[2] Stokes, Phil. Transactions 1852, p. 463.

[3] Hagenbach, Poggendorff's Annalen, 146, pp. 65, 232, 373, 508.

[4] Lubarsch, Poggendorff's Ann., 153, p. 428, 1874.

[5] Lommel, Poggendorff's Ann., 159, p. 514, 1876.

[6] Brauner, Wiener Anzeiger, 19 p. 178, 1877.

[7] Lubarsch, Wied. Ann., 6, p. 248.

[8] Lamansky, Comptes Rendus, 88, p. 1192, 1879.

It is our purpose in this paper to describe results obtained by the application of the spectrophotometer to the measurement of the fluorescence spectrum of those substances concerning the fluorescence of which, especially with reference to the validity of Stokes's law, the long-continued discussion already described arose. No attempt apparently has been made to apply the spectrophotometer to the study of fluorescence; yet it is obviously possible to determine both the limits and the maximum of a spectral region for which a curve of intensities can be plotted with far greater accuracy than by the method hitherto pursued by all observers, *i. e.*, that of attempting to set the cross-hair in the eye-piece of a spectroscope in the region of greatest brightness, or at the point where the spectrum ceases to be visible. Experimenters have perhaps been deterred from the use of the spectrophotometer because of the faintness of fluorescence spectra. It is true that fluorescent light from many substances is so weak as to preclude all measurements of its spectrum ; but it is also true, as we have found in the course of the experiments to be described, that settings can be made in cases where the brightness of the spectrum is far below that necessary to arouse the sense of color and where the presence of light can be detected only after prolonged shielding of the eye. The use of the cross-hair in such cases is out of the question, for the field is much too dim to render it visible, while every attempt to illuminate it from the side would flood the eye-piece with light sufficient to quench that under observation.

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[1] Hagenbach, Wied. Ann., 18, p. 45.

[2] Lommel, Wied. Ann., 8, p. 244, 1879.

[3] Lubarsch, Wied. Ann., 9, p. 665, 1890; also Wied. Ann., 11, p. 68, 1880.

[4] Wesendonck, Wied. Ann., 26, p. 521,

[5] Stenger, Wied. Ann., 28, p. 201.

The instrument used in most of our observations was the spectrophotometer of Lummer and Brodhun. In order to secure the greatest possible sensitiveness to weak fields of view the ocular lenses in the eye-piece were used, the eye being focussed upon the aperture in the eye-piece and not upon the face of the prism. By means of metal screens attached to the collimator slits of the instrument the length of slit was regulated so as to avoid overlapping of the spectral images and to give two contiguous spectra in the field of view. One loses by this method the advantage of the method of contrast, but the sensitiveness of the instrument for low intensities is greatly increased. Since in most cases it was desired to employ monochromatic light for the excitation of fluorescence, the spectrophotometer was employed in connection with a large spectrometer as shown in Fig. 1. The eye-piece and slit of

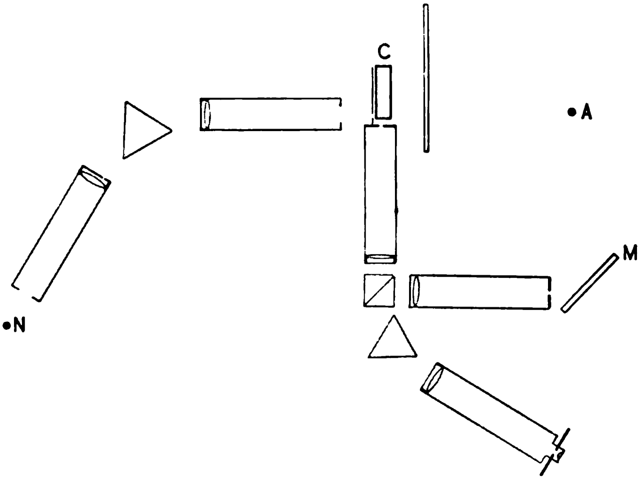

Fig. 1.

the spectrometer were removed, and in place of the latter a Nernst filament (*N*) was mounted vertically. This filament afforded a nearly linear source of light, giving a sufficiently powerful continuous spectrum. The filament was attached to the arm carrying the collimator tube so as to move with the latter and to remain in the vertical plane passing through its axis. The observing telescope was clamped, and different portions of the spectrum were brought into the field as desired by movements of the collimator tube. The liquid, the fluorescence of which was to be studied, was placed in a rectangular cell (*C*) upon one face of which a real image of the spectrum was focussed. This face of the cell was provided with a metal screen having a vertical opening 1 mm. wide through which the light used for exciting fluorescence could pass. This opening (see Fig. 2) was so placed that the exciting light entering the cell

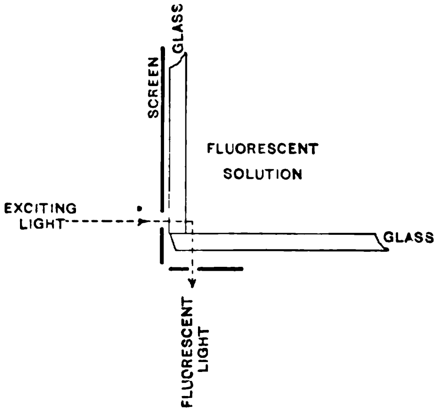

Fig. 2.

would be parallel to the adjacent face of the cell and as near to the same as practicable. In adjusting the metal screen one edge of the slit or opening was made to exactly cover the glass forming this face of the cell, as shown in the figure. The fluorescence spectrum was observed from a direction at right angles to the path of the exciting beam, and in order to bring the brightest fluorescence regions of the liquid into the field the vertical plane of the collimator of the spectrophotometer was adjusted so as to bring into the field of view the layer of liquid lying next to the face of the cell through which the exciting light entered. By this arrangement, the width of the opening through which the exciting light entered the cell and the width of the slit of the spectrophotometer each being 1 mm., the average depth of liquid within which fluorescence was produced was approximately 0.55 mm. and the average distance which the fluorescent light passed through the liquid before leaving the cell was also 0.55 mm.

The source *A* of the comparison spectrum (Fig. 1) was an acetylene flame, the light from which was reflected diffusely from the face of the block of magnesium carbonate (*M*) mounted at an angle of 45° at the end of the collimator slit. Measurements were made by varying the width of the slit until the two regions of the spectrum under observation were equally bright.

The substances specified by Lommel as belonging to his first class, in which it is possible to excite fluorescence by means of light of wave-length longer than that of a portion of the fluorescence spectrum, and in which the distribution of intensities in the fluorescence spectrum is independent of the character of the exciting light, are *naphthalin-roth*, *eosin*, and *chlorophyll.* To this list Stenger added the substance *fluorescein.* The last-named substance, on account of its intense fluorescence and the location of the fluorescent band in the middle of the spectrum, in the regions of the highest luminosity, was selected for detailed study for the purpose of testing the conclusions reached by Lommel and the other investigators mentioned in the opening paragraphs of this paper.

Ten cubic centimeters of alcohol were saturated with fluoresceïn at room temperature and the solution was filtered. To 40 c.c. of distilled water one drop of a normal solution of sodium carbonate Na_2CO_3 was added. Two parts of the concentrated alcoholic solution were then mixed with 100 parts of the water thus rendered alkaline. The fluorescence spectrum of this solution, excited by the undispersed rays of the acetylene flame, was first measured; the distribution of intensities being compared, as in nearly all our subsequent experiments, with the spectrum of the light diffusely reflected from the surface of the the block of magnesium carbonate shown in Fig. 1. The absorption spectrum of the solution was then taken, the transmission through the cell, which had a thickness of 1.1 cm., being measured by means of the spectrophotometer.

The source of the transmitted light was a second similar block of magnesium carbonate illuminated by the same acetylene flame that served for the comparison spectrum.

Much stress having been laid by some of the previous observers upon the influence of stray light, the following measurements were made. The cell was filled with distilled water, set up precisely in the position in which it had been placed in the study of the fluorescence spectrum, and similarly illuminated by means of the acetylene flame. No measurable stray light was found, but an exceedingly weak fluorescence spectrum due to the glass walls of the cell was detected. Since the maximum of the fluorescence spectrum of the glass was found to lie further to the violet than the fluorescence spectrum of the fluoresceïn, and since moreover it was of scarcely measurable intensity, it was not deemed necessary to take further cognizance of these sources of error.

To determine the fluorescence spectrum of the solution when excited by monochromatic light, a mercury arc-light of the Lummer pattern was set up in front of the slit of the spectrometer. It was found that the violet lines from the spectrum of this arc produced fluorescence corresponding, as regards the position of the maximum and the general form, with the curve previously obtained by means of the light of the acetylene flame, but that the green line ($\lambda = .575$) excited no fluorescence. This latter result was to be expected since this light lies altogether outside of the absorption band of the solution in a region for which almost complete transparency exists. The spectrum of the acetylene flame was subsequently tried as an exciting source, but it was too weak to give easily measurable intensities of fluorescence. The slit of the spectrometer was then removed and a Nernst filament was mounted in the axis of the collimator tube as described in the specification of the apparatus and shown in Fig. 1. This filament was found to be of abundant brilliancy. It was maintained at constant brightness by means of a variable resistance, which was adjusted whenever the fluctuations of an ammeter placed in the electric circuit indicated it to be necessary.

Measurements of the fluorescence spectrum of the solution were made by means of the spectrum of the Nernst filament using as exciting light three nearly monochromatic regions of wave-length

$\lambda = .518\,\mu$ to $.536\,\mu$, $\lambda = .487\,\mu$ to $.502\,\mu$ and $\lambda = .460\,\mu$ to $.471\,\mu$. The curves thus obtained are plotted in Fig. 3, together with the curve of transmission for the solution. It will be seen from this figure that the maximum of intensity of the fluorescence spectrum in these three cases lies in the same region at $.517\,\mu$ and that there is no evidence of any shifting of the fluorescence spectrum with the wave-length of the exciting light. It is obvious, moreover, that not only is it possible in the case of this solution to obtain fluorescence of refrangibility less than that of the exciting light, but that in the case of the curve marked *A* the maximum of the fluorescence spectrum is of shorter wave-length than the shortest wave-length used in excitation. These curves likewise agree fully in character and as regards the position of their maximum, with that for the fluorescence spectrum of the same solution when excited by the undispersed light of the acetylene flame. (Not shown in the figure.)

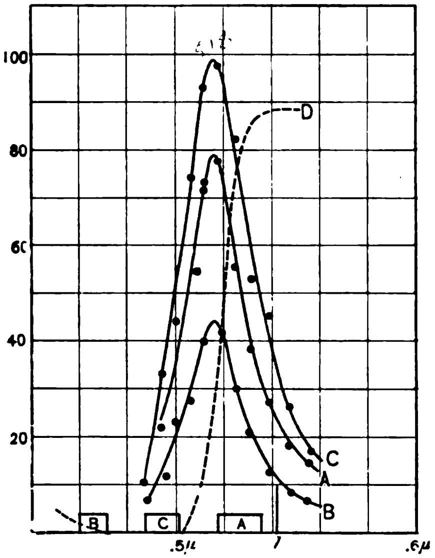

Fig. 3.

Fluoresceïn. Fluorescence spectra obtained when the exciting light lies in different regions of the spectrum. For curve *A*, the exciting light was confined to the region marked *A* on the horizontal axis, etc. Vertical scales arbitrary.

These curves for the fluorescence spectrum do not correspond precisely with the typical curve, meaning by that term the curve representing the distribution of intensities in the fluorescence spectrum of the surface layer of the fluorescing liquid. It is possible, however, in the case of a non-turbid medium, to compute from the observed curve the approximate form of the typical curve. Fig. 4 shows graphically the result of such a computation.[1] Curve *A* gives the transmission of a glass cell containing a layer 1.1 cm. in thickness of the fluoresceïn solution. The dotted curve of similar form gives the transmission corrected for losses in the cell when filled with distilled water. From this by the well-known law of variation of absorption with the thickness, the curve *D* is found for a layer 0.055 cm. in thickness, which is the estimated mean distance through the solution which the fluorescent light passes before entering the slit of the spectrophotometer. The curve *B* is the observed curve of the distribution of the intensities in the fluorescence spectrum, and from this was computed the curve *E*, which represents, as nearly as the accuracy of the data will allow, the typical curve for this

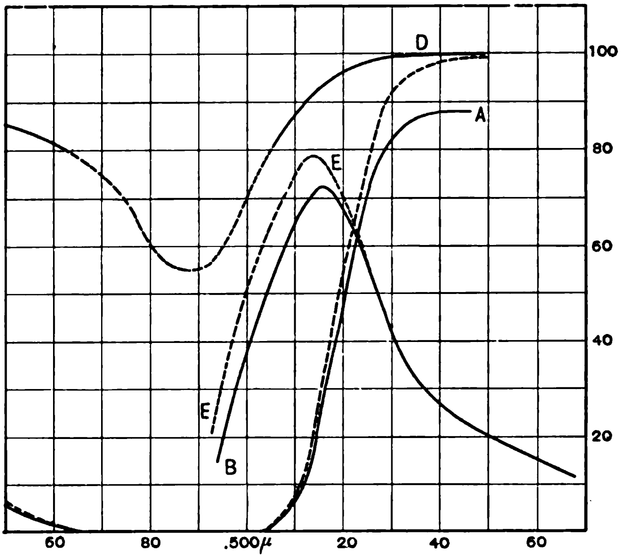

Fig. 4.

Fluorescein: typical fluorescence spectrum (*E E*).

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[1] In this figure and in Figs. 5, 6, 7 and 8 the scale of wave lengths has been doubled.

substance, corrected for absorption. It will be seen that in the case of this solution, under the conditions of the measurements, the absorption of the fluorescent light by the solution produces only a slight shifting of the maximum toward the shorter wavelengths. When the fluorescent light passes through a considerable layer of the solution the effects of absorption are much more marked and there is a decided change of color. When a thin layer of the solution of fluoresceïn is viewed by reflected light its color is green, whereas the fluorescence of a mass of the liquid appears decidedly yellowish. This change is shown graphically in the curves of Fig. 5. In this figure *A* is the transmission curve of the solution; *B* is the observed curve of fluorescence when the slit through which the excited light enters the cell is placed so that the fluorescent light passes through .055 cm. of the solution before exit; and *C* is the fluorescence curve when the slit is shifted to such a position that the fluorescent light passes through 1 cm. of the solution. It will be seen that the maximum is shifted from .516 μ to .522 μ, and that while the two curves are nearly coincident on the side towards the red the values on the other side of the curve fall off very rapidly as the result of the increased absorption. The

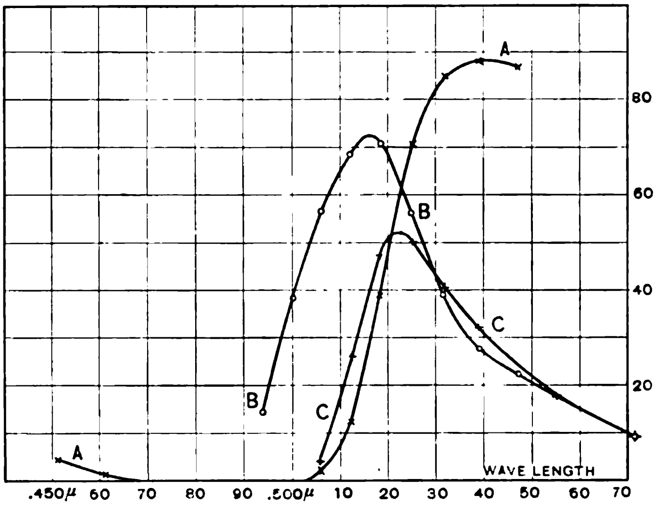

Fig. 5.

Fluoresceïn. Effect of absorption upon the fluorescence spectrum.

boundary of the fluorescence spectrum towards the violet in the one case would lie at about wave-length .505 μ, whereas in the thinner layer it would be visible to at least .490 μ. It is obvious that the color of the fluorescence in the latter case will contain a great excess of green.

The effect of diluting the fluorescent solution is similar to that of diminishing the distance through which the light passes. The results of observation upon a solution of fluoresceïn, diluted until the intensity of the fluorescence spectrum was diminished as far as would permit of satisfactory readings, are shown in Fig. 6. The curve *AA* represents the transmission of the cell filled with the dilute solution and *BB* is the distribution curve of its fluorescence spectrum. The dotted lines show the corresponding transmission curve and a portion of the fluorescence curve for the solution before dilution. It will be noted that in this case, as in the case of the comparison of thick and thin layers of a given solution, the curves are coincident toward the red, but that the dilute solution has its maximum shifted towards the green ; also that the ordinates on this side of the curve show an increase indicative of the change of color, which, as is well known, is always observed as the result of diluting the fluorescent solutions of this substance.

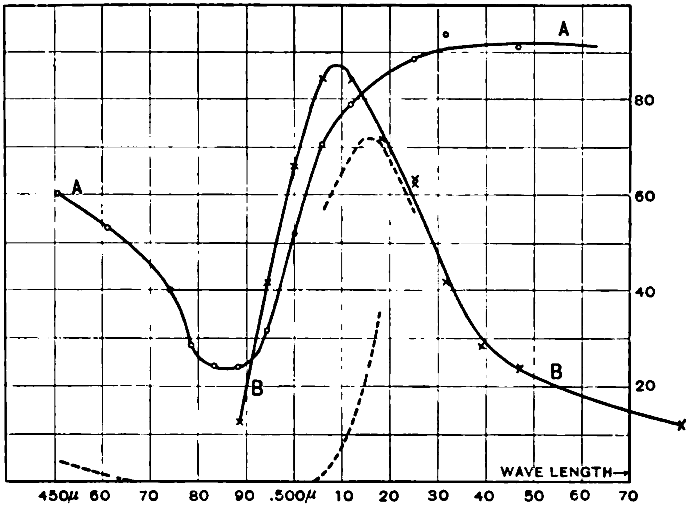

Fig. 6.

Fluoresceïn. Effect of dilution upon the fluorescence spectrum.

Although, as has been shown in Figs. 4 and 5, the modifications produced by absorption in the curves of the fluorescence spectrum may be very marked, the effect of absorption diminishes rapidly with dilution of the solution. If we apply the correction for absorption, for example, to the curve for the dilute solution in Fig. 6 we find as is indicated in Fig. 7 that the change is insignificant. In this figure *C* is the observed curve for the fluorescence of the dilute solution, *A* the transmission curve of a layer 1.1 cm. in thickness, and *B* the computed curve for the transmission of the mean layer of liquid through which the fluorescent light has to pass. The correction for this absorption is indicated by means of the dotted line.

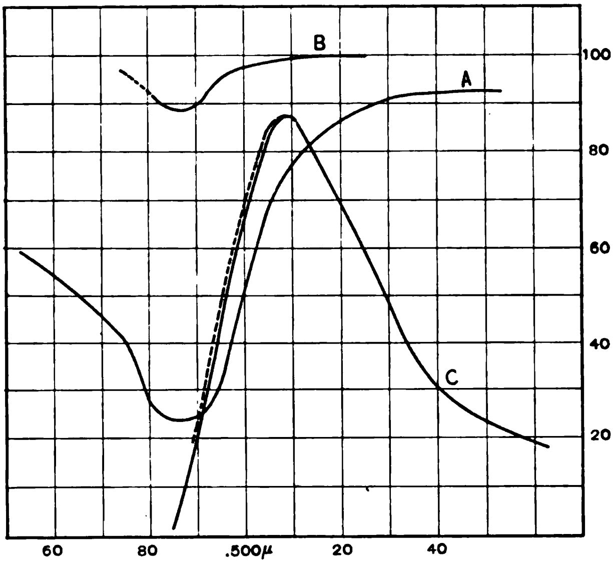

Fig. 7.

Fluorescein. Typical fluorescence spectrum for dilute solution.

It having been established that the fluorescence of bodies of this class is independent, as regards the distribution of intensities, of the wave-length of the exciting source, it would be of interest to inquire whether the fluorescent energy for a given wave-length of the fluorescence spectrum varies with the wave-length of the exciting light, the energy of which is constant, or whether it depends only upon the energy. The rigorous determination of these relations involves a knowledge of the distribution of energy in the spectrum of the exciting source, a difficult matter to determine with accuracy for the shorter wave-lengths of the visible spectrum. The curve shown in Fig. 8 may, however, be of some interest in this connection. It represents the intensity of fluorescence, taken at the maximum of the fluorescence spectrum of the solution of fluoresceïn, as a function of the wave-length of the exciting light. Curve *A* was taken with the Nernst filament as a source, curve *B* with the acetylene flame. The dotted line shows the absorption band for a layer of the solution 1.1 cm. thick. It will be seen that fluorescence begins approximately at the wave-length at which the solution seems to be transparent, and that the maximum lies well within the absorption band but is shifted to the red. The longer wave-lengths within the band are more effective on account of their greater energy. The difference in the form of the curves *A* and *B* is probably ascribable to the different distributions of energy in the spectra of the sources of light employed.

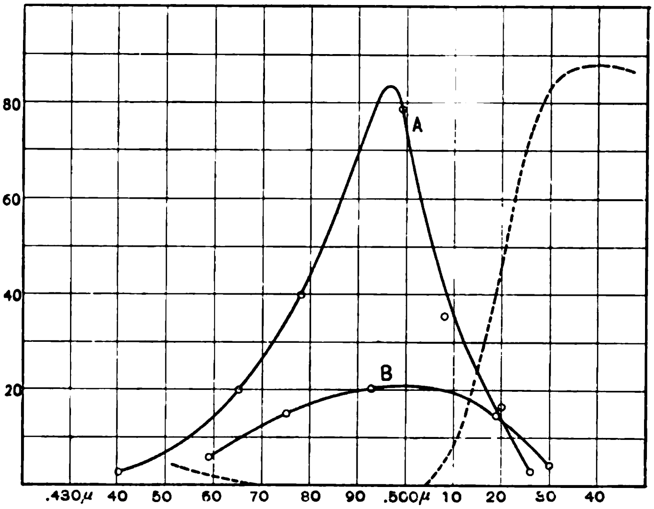

Fig. 8.

Fluoresceïn. Intensity of fluorescence as a function of wave length of exciting light. A refers to Nernst glower as source, B to acetylene flame.

In addition to the measurements on fluoresceïn the positions of the fluorescence spectra of solutions of eosin and naphthalin-roth were determined by the method already described, and the transmission curves of the solutions were taken. Dilute solutions in alcohol were made, that of the naphthalin-roth being about $\frac{1}{200}$ saturated. The results obtained with these solutions, which are shown in Figs. 9 and 10, afford additional corroboration of the statements of Lommel. They are indeed in every respect analogous to those obtained with fluorescein and lead to the same conclusions. Each solution was excited by three distinct regions of the spectrum, one lying as far toward the red as practicable, one towards the blue and one at an intermediate wave-length. Curves showing the distribution of intensities in the three spectra thus produced are shown in the figures and it will be noted that, as in the corresponding curves for fluorescein, the position of the maximum is entirely independent of the wave-length of the exciting light and that the general character of the curve remains unchanged. In the case of these two solutions, as in that of fluorescein, it was possible to obtain a measurable amount of fluorescence by the use of light of

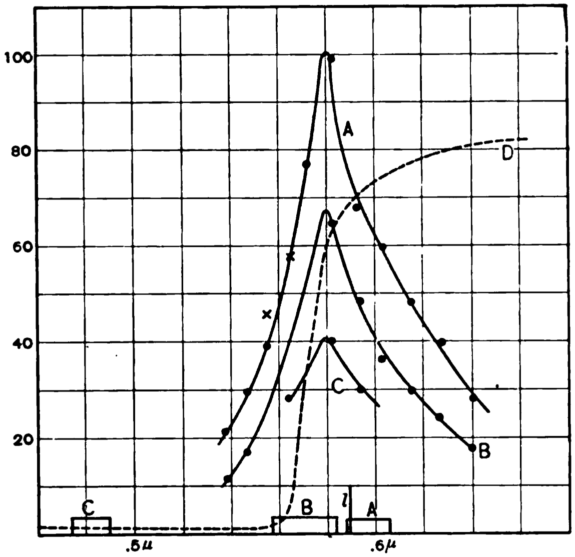

Fig. 9.

Eosin. Fluorescence spectra observed when the exciting light lies in different regions of the spectrum. Curve *A* was obtained when the exciting light was confined to the region marked *A* on the axis of wave-lengths, etc. Vertical scales arbitrary.

greater wave-length than that of the maximum of the fluorescence spectrum. The form of the fluorescence curve is very similar for these three substances but each has its own place in the spectrum. The maximum for fluorescein (Fig. 3) is at .517 *μ*, that for eosin at .580 *μ* and that for naphthalin-roth at .594 *μ*. The position of the maximum of these three curves with reference to the absorption band appears to vary with the different substances. The maximum for eosin coincides approximately with the infra-edge of the absorption band; that for fluorescein lies slightly (about .05 *μ*) towards the violet, while the maximum for naphthalin-roth is much further displaced towards the short wave-lengths.

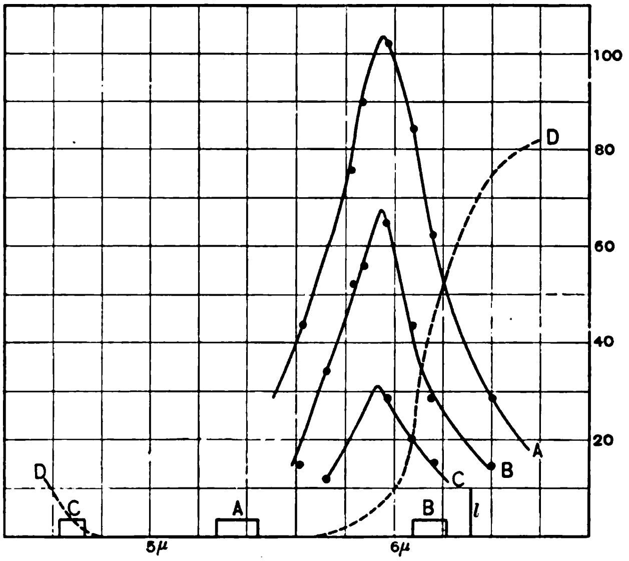

Fig. 10.

Naphthalin-roth. Fluorescence spectra obtained when the exciting light lies in different regions of the spectrum. Curve *A* was obtained when the exciting light was confined to the region marked *A*; etc. Vertical scales arbitrary.

Lommel's contention that it is possible to excite fluorescence in eosin by means of the light of the sodium flame is fully confirmed by the data plotted in Fig. 9, from which it will be seen that the exciting light by means of which curve *A* was obtained had a mean wave-length almost precisely equal to that of the sodium lines. Since it was found possible by means of light, all of which was of greater wave-length than the maximum of the fluorescence spectrum, to produce fluorescence of sufficient strength for measurement with the spectrophotometer, it follows that *observable* fluorescence can be produced by light of even greater wave-length than that recorded in our diagram.

We deem the evidence already given in the foregoing paragraphs to be conclusive, so far as these substances are concerned; but in view of the differences of opinion among physicists as regards the validity of Stokes's law we venture to add the following description of a determination of the wave-length of the least refrangible monochromatic light which we found capable of exciting fluorescence in the three solutions with which this paper deals.

Since some writers have laid great stress upon the errors due to stray light, two different methods were employed of avoiding it. In the first the exciting light was passed through a solution of the substance to be examined before dispersion, thus filtering out those rays particularly active in producing fluorescence. The filtered light was then dispersed by means of the large spectroscope already described, and a second solution was subjected to an isolated, nearly monochromatic, region of the spectrum. The wave-length of this region was increased until the last trace of fluorescence, observed directly with the eye, was about to disappear. To distinguish between fluorescence and the presence of light diffused from small particles, the light was viewed at an angle of 90° through a Nicol prism, by which means diffuse light was completely excluded. The limit of excitation thus determined lay, as had been anticipated, further to the red than in the cases where a *spectrophotometrically measurable* fluorescence had been obtained, excepting in the case of eosin, where it was found to coincide almost exactly with the ultra-edge of the band used in exciting the spectrum shown in curve *A* (Fig. 9).

The second method consisted in sending the isolated region of the dispersed light to be used for excitation through a second spectroscope and determining as before the limit of excitability. This method of removing stray light has been extensively used and is well known to be effectual. The source of light in both cases was an arc-light.

The results obtained by these two methods were identical. They were as follows :

TABLE.

Substance.	Maximum Wave-length Exciting Observable Fluorescence.
Fluorescein,	.542
Eosin,	.589
Naphthalin-roth,	.632

These wave-lengths, all of which lie far to the red from the maximum of the fluorescence spectrum, are indicated in Figs. 3, 8, and 9 by means of the vertical lines marked *l*.

Measurements upon other fluorescent substances, and especially upon those which Lommel regarded as not belonging to his first class, are in progress and the results will be given in a subsequent communication.

PHYSICAL LABORATORY, CORNELL UNIVERSITY,
December, 1903.

THE VISCOSITY COEFFICIENT OF AIR, WITH AN INQUIRY INTO THE EFFECT OF THE RÖNTGEN RAYS THEREON.

By Frederick G. Reynolds.

I. Historical.

THE phenomena of viscosity have claimed the attention of investigators for many years; but while the general truths may be said to be settled, there have always existed many differences of detail in which one may find a justification for further effort in the same field.

By the viscosity of a gas is meant the resistance which it offers to a continuous change of form divided by the rate at which that change is effected. The coefficient of viscosity may perhaps be best understood by considering a stratum of the gas infinite in extent. If this stratum were enclosed by two parallel planes at a distance d centimeters from each other and if one of these planes were to move parallel to the other with a velocity of v centimeters per second, keeping always in the same direction, till the gas embraced takes up its final velocity thus imparted, this velocity would decrease uniformly as we pass from the moving plane towards the other. If again the strata in contact with the two planes have the same velocity as the planes themselves, the strata will decrease in velocity v/d centimeters per second for every centimeter we depart from the moving plane. The friction between any two contiguous strata will then be the same as between either plane and the stratum in contact with it. If this friction be denoted by a tangential force F on every square centimeter of surface then $F = Uv/d$ where U is the coefficient of viscosity of the gas. The measurement of the internal friction or viscosity of a gas is the determination of the value of this coefficient.

The property which enables one layer to drag along another might in liquids be looked upon as a cohesion acting in opposition to the motion, but in the case of a gas we must look for another explanation. In the light of the kinetic theory we look upon the gas as manifesting itself by the very rapid motion of its molecules. When two layers are moving therefore with unequal velocities, the molecules from the faster moving layer penetrate the slower moving one with their faster forward velocity and vice versa, so a measure of the friction would be the momentum which is thus carried over. The heat motion of the molecules is so great (being at 0° C., a mean velocity of 447 meters per second), that it is not affected by the comparatively slow forward motion of the molecules. It would naturally follow that this friction would increase with an increase of the temperature, for the speed of the molecules increases with the temperature being proportional to the square root of the absolute temperature. That the friction is independent of the density seems paradoxical at first, but the theory is at least justified when we consider that the transfer is made by the molecules and is greater as their number and activity are greater hence as the density is greater, but at the same time the transfer takes place in layers whose distance apart may be traversed by the molecules and as the density increases, this distance is restricted so that it is possible that the combined result of the two causes should produce a constant effect.

The methods of approaching and handling the investigations into the viscosity of fluids, both theoretical and practical may be divided into four general classes :

I. By their transpiration through capillary tubes. In this phase of the investigation Poiseuille[1] and Graham[2] were the pioneers, the former as to liquids and the latter as to gases.

II. By the swinging of pendulums. This method was followed by Baily.[3] Bessel[4] and Du Buat[5] whose work is discussed in a paper by Stokes[6] "On the internal Friction of Fluids on the Motion of Pendulums."

III. By the torsional vibrations of an immersed disc, first adopted by Coulomb.[7]

[1] Mém. de Savants Étrangers, 1846, IX., p. 433.

[2] Phil., Trans., 1846, CXXXVI., p. 573; 1849, CXXXIX., p. 349.

[3] Phil. Trans., 1832.

[4] Berlin Acad., 1826

[5] Principes d'Hydraulique, 1786.

[6] Cambridge Phil. Trans., 1850, IX., pt. 2

[7] Mém. de l'Institut National, III., p. 246.

IV. By the torsional vibrations of a vessel filled with the fluid in question. This might be considered as a development of the preceding method.[1]

Each method seems to have its practical and theoretical advantages and disadvantages and the discordant results attending the early efforts in each have since been brought more closely into harmony through criticism and refinements of method. In speaking of the transpiration and torsion methods Meyer remarks of the discrepancies "als begründet in den Annahmen, welche zur Gewinnung brauchbarer Formeln in die theoretische Entwickelung eingeführt würden; die dabei eintretenden Vernächlässigungen wären in dem Falle schwingender Scheiben derart, dass der Coefficient zu gross, in dem Falle des Ausflusses durch Capillarröhren derart dass er zu klein erhalten müsste; die wahren Werthe würden also zwischen der Resultaten dieser beiden Methoden liegen." Which method comes nearer to the truth is not decided but the possible objection to the transpiration experiments lies in the difficulty of measurement of the diameters of the tubes and also in the fact that on account of the smallness of the bore one cannot be certain that the action between the molecules of the gas and of the substance of the tube does not affect the result. The pendulum method seems to be considered capable of great accuracy, but in the theory applicable to it Baily made the error of considering that the viscosity is dependent on the density. A revision of his results on the basis of a correct hypothesis has been promised but does not seem to have been made. The difficulties or objections connected with the method of a vibrating disc seem to be less than in the transpiration method and it may be for this reason that it has been the method generally selected by the later investigators; but the trouble here lies in the necessity of accounting properly for the effect of the motion of the medium near the edge of the discs. As a result of Maxwell's[2] analysis and deductions, given in 1860, both he and Meyer[3] started to practically demonstrate the truth of the same, using as a basis of their investigations the method adopted by Coulomb, but Meyer altered the earlier method in so far as to substitute three oscillating discs with a common axis instead of the one used by Coulomb. These plates were so arranged that it was possible to separate them, thereby exposing six surfaces, or to place them together, exposing only the two. In this way the friction on the exposed parts of the hanging system such as the mirror, etc., as well as the internal friction of the wire itself could be eliminated by considering the difference of the effects obtained when the plates were apart and together. Maxwell improved on this by inserting four fixed plates between the moving ones, which had the effect of causing the friction of the gas to exert a greater resistance and therefore one more easily measured, an advantage which was immediately recognized by Meyer[1] himself. A further advantage of Maxwell's method lies in the fact that his deductions give the viscosity coefficient directly, whereas Meyer's deductions lead to the square root which would cause the effect of any error to be increased. As a consequence Maxwell's results showed a better agreement in the effort to verify the independence of the coefficient and the pressure within the range of his observations, viz: from one to one sixtieth atmospheres. In 1887 as a result of a correction suggested by Koenig[2] an improvement was made by Meyer in his method and he calculated his results again on the improved theory.[3]

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[1] Helmholtz and Pietrowski, Sitzungsber. der kk. Akad., April, 1860.

[2] Phil. Mag., 1860, (4), XIX., p. 31; Phil. Trans., 1866, CLVI., p. 249.

[3] Pogg. Ann., 1865, CXXV., p. 177.

This independence of the viscosity and the pressure cannot be expected to hold in the limiting cases, as would follow from a consideration of the theory. The density and the free path enter we have seen as factors but when the former approaches 0 the latter approaches ∞ which would cause this phenomenon to fall outside of a development where only finite densities and free paths are considered.

Investigations on this point at low pressure were taken up by Kundt and Warburg,[4] who followed Maxwell's methods and found that below a pressure of one sixtieth atmosphere there was a marked diminution in the logarithmic decrement from which the viscosity coefficient is calculated. They however found an explanation of this in a phenomenon which they called slipping or (external friction) by which is meant the sliding of the medium along the bounding surface as distinguished from the sliding of one layer of the medium along another layer; and they explained this falling off as not caused by a decrease of the coefficient of viscosity but by an increase of the slipping at the lower pressure. Even a highly polished surface must in comparison with the molecules of the gas be considered rough, and under ordinary pressures a sliding along this, especially since the forward motion is very slow, is practically impossible, but this would not be the case in a very rare medium. By the term coefficient of slip they designated the ratio of the internal to the external friction, with the result that between the pressures of .6 and 20 millimeters of mercury the value of the coefficient of slip was found to be inversely proportional to the density of the gas and very nearly equal to the free path of the molecules. Therefore the external friction is directly proportional to the density. Warburg[1] experimented further on the external friction by the transpiration method and obtained smaller values for the coefficient of slip but Breitenbach[2] later obtained results nearer the earlier ones.

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[1] Pogg. Ann., 1871, CXLIII., p. 14.

[2] Wied. Ann., 1887, XXXII., p. 193.

[3] Wied. Ann., XXXII., p. 642; Sitzungber. d. Münchener Akad., 1887, XVII., p. 343.

[4] Monatsber. d. Berl. Akad., 1875, p. 160; Pogg. Ann., 1875, CLV., pp. 337, 525.

The correctness of this explanation of Kundt and Warburg for the sudden falling off the logarithmic decrement was later proven by Crookes[3] on a theory developed by Stokes,[4] wherein he used his vacuum tubes with vertically suspended strips of mica thereby excluding the possibility of any external friction. The results of these investigations show the independence of viscosity and pressure down to pressures so low as to be no longer accurately measured. However, at much higher vacuums there is a break in the constancy.

At extremely high pressures the law does not hold, but this might also be expected from the assumptions in the theory. Start-

[1] Pogg. Ann., 1876, CLIX., p. 399.

[2] Wied. Ann., 1899, LXVII., p. 826.

[3] Phil. Trans, 1881, CLXXII., p. 387.

[4] Phil. Trans., 1881, CLXXII, p. 435.

ing with the hypothesis that the particles traverse straight paths between their successive encounters with each other, the curved paths traversed during the period of actual encounter would be negligibly small, at ordinary densities or at low densities; but this would not be the case when the density becomes very great. The law considers the molecules unchangeable and the dissociation of the molecules under this extreme condition may contribute to this variation. This would be particularly true in the consideration of vapors. Warburg and Babo[1] have shown in the case of carbonic acid that the coefficient of viscosity increases with the density at pressures from 30 to 120 atmospheres, which law seems to hold for other gases as well.

In 1866 Meyer[2] published a theory where in assuming the independence of pressure upon the friction, he gave a law governing the speed of flow of gases through capillary tubes which corresponded with the law found by Poiseuille for liquids and which, by considering the amount of gas transpired in a given time leads to the value of the coefficient of friction. His calculations from the results of Graham's observations proved the correctness of his assumption. He obtained for the coefficient of viscosity of the air at 0° C. the values .000171, .000170, .000174 and he also gave the coefficients for nineteen other gases. Obermayer[3], Puluj[4] and Mutel following this method obtained for air the values .000167, .000180, .000172 respectively.

As to the fact of the increase of the viscosity with the increase of the temperature there can be no doubt, but as to the rate of such change there is not such an agreement among the different investigators. Maxwell first put it as increasing directly as the absolute temperature or proportional to $(1 + a\vartheta)$ where ϑ is the temperature from the freezing point and a is the coefficient of expansion. Later experiments show that for air at least it does not increase so rapidly. Efforts were made to represent the change by a factor of the form $(1 + a\vartheta)^n$ where n was first given as three fourths but later Barus[5] adopting the transpiration method and with a range of temperature from 0° to 1300° gave to *n* the value two thirds for air and hydrogen. Different values were found by others for other gases and Wiedeman[1] found that *n* became smaller with the increase of temperature, a fact also found by Holman.[2] Schuman[3] however chose to represent the change by a formula consisting of two factors $(1 + \gamma\vartheta)^2\sqrt{1 + a\vartheta}$ from the consideration that the viscosity is dependent upon two things, the molecular free path and the molecular speed; and while this satisfied his own observations founded upon Maxwell's method, it did not agree with those of Barus. Sutherland[4] taking into consideration the *apparent* sphere of action of the molecules as distinguished from the real sphere of action, changed the first factor and represented the change by the equation,

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[1] Weid. Ann., 1882, XVII., p. 390; Sitz. d. Berl. Akad., 1882, p. 509.

[2] Pogg. Ann., 1866, CXXVII., pp. 253, 353.

[3] Carl's Rep., 1876, XII., p. 13.

[4] Wien. Ber., 1874, LXIX., (2), p. 287; LXX. (2), p. 213.

[5] Bull. of the U. S. Geol. Surv., No. 54, Washington, 1889; Wied. Ann., 1889, XXXVI., p. 358.

$$\eta = \eta_0 \frac{(1 + ac)}{\left(1 + \frac{c}{\theta}\right)} \cdot \sqrt{1 + a\vartheta},$$

θ being the absolute temperature, a the coefficient of expansion and c a constant depending on the attractive forces exerted between the molecules when near together. With this he found results agreeing well with Barus and Holman.

Vapors as distinguished from gases proper have also been the subject of observations to determine if they follow the laws of gases as to viscosity. In these researches L. Meyer[5] and Koch[6] have followed the transpiration method while Puluj[7] and Schumann[8] have used the oscillation method with the result that at ordinary pressures, like true gases the coefficient of viscosity is independent of the pressure. However the formulæ given for true gases do not here represent exactly the change with the temperature and it seems that the viscosity changes in a much larger ratio. Attempts to justify this disagreement have been made wherein the causes which make the laws of a perfect gas differ from the laws of vapors are used for a basis of argument. Of these perhaps the principal one which might be mentioned is the phenomenon of dissociation.

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[1] Arch. d. Sc. Phys. et Nat., 1876, LVI., p. 273.

[2] Proc. Amer. Acad., Boston, 1877, XII., p. 1; Phil. Mag. (5), III., p. 81; XXI., p. 199.

[3] Wied. Ann., 1884, XXIII., p. 353.

[4] Phil. Mag., 1893, (5), 202, p. 507.

[5] Wied. Ann., 1879, VII., p. 497; 1881, XIII., p. 1; 1882, XVI., pp. 369, 394.

[6] Wied. Ann., 1883, XIX., p. 857.

[7] Wien. Ber., 1878, LXXVIII., (2), p. 279; Carl's Report, 1878, XIV., p. 573.

[8] Wied. Ann., 1884, XXIII., p. 353.

The question of the effect of electric and magnetic fields on the viscosity of a gas has not as yet been very satisfactorily determined, but that these cause no effect would appear from the results of Pagliani[1] and Noack.[2] Koenig[3] oscillated crystal spheres in a magnetic field but the effect on the coefficient of viscosity was not apparently considered. Quincke[4] also investigated the viscosity of fluids in the electric field, showing an increase without any apparent change in the period of swing of the spheres. To these results however objection was made by Boltzman.[5] The results of the efforts of investigators to determine the Coefficient of Viscosity of the Air, with the methods used by them may be seen by the table on p. 427.

As a consequence of the corrections in theory and through the refinements of process the results of the different methods while they varied widely at the start, have been brought into closer harmony. Since no new method differing in principle from these has been given, the only available way of testing the correctness of the results is in a variation of the methods at hand. The method of torsional vibrations seem to permit of a wider range of variation and therefore to be best suited to such a purpose. The objections to the use of discs however has been mentioned as lying in the allowance to be made for the action at the edge of the disc; but the improvement of method in substituting several in place of the one partly obviated this. This objection would not of course hold if a spherical surface were substituted and for this reason as well as that symmetry renders possible a rigorous theoretical development, the sphere or spherical shell seems best suited to answer the requirements.

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[1] Ac. Torino, 1885, XX., p. 615; 1887, XXII., p. 1.

[2] Wied. Ann., 1886, XXVII., p. 289.

[3] Wied. Ann., 1887, XXXI., p. 273.

[4] Wied. Ann., 1897, LXII., p. 1.

[5] Wied. Ann., 1897, LX., p 399.

Previous Determinations of the Coefficient of Viscosity of Air.

Investigator.	Method.	Coef. C. G. S.	Temp.	Reference.
Stokes	Baily's Pendulum	.000104		
Meyer	Oscillation	.000353	0	Crelle's Jour., 59, p. 229.
“	Bessel's Exper.	.000273		
“	Girault's “	.000384		
“	“ “	.000360	18	
“	Oscillation (2°)	.000333	8.3	Pogg. Ann., 1871, CXLIII., p. 14.
“	“	.000323	21.5	
“	“	.000366	34.4	
“	Transpiration	.000168	0	Pogg. Ann., 1873, CXLVIII., pp. 37, 203.
“	“	.000174	0	
Maxwell	Oscillation	.000200	18	Phil. Trans., 1866, 156, p. 249.
Puluj	Transpiration	.000179	0	Wien. Sitz., Abth. 2, 1874, LXIX., p. 287.
				Wien. Sitz., Abth. 2, 1874, LXX., p. 243.
Von Obermayer	“	.000171	0	Carl's Rep., 1876, XII., p. 13.
“	“	.000168	0	Wien. Sitz., 1875, LXXI., p. 281; 1876, LXXIII., p. 433.
Schumann	Oscillation	.000168	0	Wied. Ann., 1884, XXIII., p. 353.
Schneebeli	Transpiration	.000171	0	Arch. des. Sci. Phys. et Nat. Geneve, 1885 (3), XIV., p. 197.
Tomlinson	Oscillation (Cylinder)	.000179	12.02	Phil. Trans. (2), 1886, CLXXVII., p. 768.
“	“	.000176	10.64	
“	“	.000177	14.63	
“	“	.000178	11.69	
“	“ (Spheres)	.000176	9.97	

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(*To be continued.*)

THE EFFECT OF PRESSURE ON MAGNETIC INDUCTION.

By Fannie Cornelia Frisbie.

THE reciprocal relations existing between the change in shape or size of a body and its magnetization are so striking that they excite immediate interest, and make a thorough investigation of these relations necessary before a satisfactory theoretical explanation of the phenomena of magnetization can be given. As different investigators of the effect of hydrostatic pressure on magnetic permeability have obtained contradictory results, it was thought worth while to undertake the problem in a new way. Before describing the method used it will be well to survey briefly the theoretical and the experimental work already done.

On the supposition that Poisson's theory of induced magnetism for rigid bodies in a vacuum is correct, Helmholtz[1] (1881) deduced, with the aid of the principle of conservation of energy, expressions for the forces which act between the particles of magnetic or dialectric polarized bodies. These agreed with those of Clerk Maxwell[2] and Sir Wm. Thomson, except that they contained, beside the coefficient of induction, a constant which depends upon the nature of the medium, and which is determined by the change which it undergoes on change of density. Kirchoff[3] (1884) introduced another constant which makes it possible to express the change experienced by induction through dilations which are different in different directions, thus applying to solid bodies as well as to fluids.

Drude[4] has shown from purely theoretical considerations that since the shape of a body is altered by magnetization, any alteration of shape or size should change the value of the coefficient of magnetic permeability of the body.

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[1] Wied. Ann., 13, p. 400; Abhandlung, I., p. 798.

[2] Electricity and Magnetism, § 644.

[3] Wied. Ann., vol. 24, p. 52; Gesammelte Abhandlung, Nachtrag, p. 91.

[4] Physik des Aethers, p. 156.

It is found that change in the state of magnetism of a body alters its shape and size in various ways depending upon the strength of the magnetizing field.[1] The effect is to increase the length of an iron rod or ring in small magnetizing fields, as the field is made stronger the increase reaches a maximum, falls to zero, and for still stronger fields there is a diminution in length. It is found that accompanying the increase in length there is a decrease in thickness, and this led the early investigators to conclude that there was no volume change due to magnetization; later experimenters[2] have, however, found a rapid increase of volume with H, the magetizing force, to a certain point after which it increases asymptotically.

Since there was found to be a deformation of a body with an alteration of its magnetization, it was natural that one should next look for a reciprocal relation between the two phenomena, and it was found that a long thin rod under longitudinal tension underwent an increase of magnetization[3] until the magnetic moment reached a certain amount, after which further pull produced a diminution. Longitudinal and also transverse pressure produced effects opposite to those of longitudinal stretch.

The effects of hydrostatic pressure were investigated (1882) by Wassmuth[4] who placed the iron rod inside a thick walled tube which he filled with mercury. Pressure was obtained by the expansion of the mercury when heated by means of warm water. One end of the glass tube was drawn out to a capillary from which increase of pressure was observed. The glass tube was surrounded by a solenoid which exerted a nearly uniform magnetizing force upon the iron rod. The intensity of magnetization was learned by the deflection of a mirror. He found that with increasing hydrostatic pressure the temporary moment in general decreased, and only increased for magnetizations which lie near the maximum. He estimated that he had about ten atmosphere pressure. Tomlinson[1] (1887) investigated the same subject and obtained negative results. He found no perceptible change either in the magnetic permeability of soft iron or in the permanent magnetism of hard steel; but at the beginning or at the end of the hydrostatic pressure, as similarly with longitudinal compression and extension, a part of the residual magnetism vanished. Nagaoka and Honda again obtained positive results, but these were not in agreement with those of Wassmuth. They had two similar brass tubes containing the rods to be examined. About the tubes were wound the magnetizing solenoids. The tubes were filled with water and pressure was obtained by means of a Cailletet pump. A magnetometer placed symmetrically with regard to the rods was adjusted until there was no deflection, then pressure was applied to one, and the change in magnetization produced a deflection of the magnetometer which could be observed. They used rods and ovoids of soft iron and found a decrease in the magnetization with pressure up to 250 atmospheres, using a magnetizing field, *H*, from 5–5.5 c.g.s. units. They calculated from data furnished by other parts of their series of experiments on magnetostriction the result to which Kirchoft's theory leads and found that the theory calls for an increase. Their series of experiments agreed with theory for the most part, but in regard to the effect of hydrostatic pressure there was not the same accord between experiment and theory. Unfortunately they make no statement about the condition of the iron and its previous treatment.

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[1] Wiedemann, Lehre von der Electricität, III., pp. 703–714. Joule, Phil. Mag., (3) 30, pp. 76, 225, 1847; reprint of papers, p. 235. Cantonne, Mem. d'R. Accad., vol. 6, p. 487, 1890. Bidwell, Proc. Roy. Soc., 40, pp. 109, 257, 1886; 43, p. 406, 1888; 47, pp. 46–49, 1890; 56, p. 94, 1894; Phil. Trans., vol. 179 A, 1888, p. 205; Beiblätter, 12, p. 600. Knott, Proc. Roy. Soc. Edin., 19, p. 249, 1892; 20, pp. 290, 295, 334, 1893–5; Trans. Roy. Soc. Edin., 38, p. 527, 1896.

[2] Nagaoka and Honda, Phil. Mag., 5, vol. 37, p. 131, 1894; 5, vol. 46, p. 261, 1898; Beibl. 18, p. 595; Wied. Ann., vol. 53, p. 487, 1894.

[3] Wiedemann, Lehre von der Electricität, III., pp. 698–703. Wertheim, Compt. Rend., 35, p. 702, 1852; Ann. de Chim. et Phys. (3), 50, p. 385, 1857. Matteucci, Ann. de Chim. et Phys. (3), 53, p. 416, 1858. Villari, Pogg. Ann., 126, p. 67, 1868. Sir Wm. Thomson, Phil. Trans., 166, p. 693, 1876; Beibl. 2, pp. 362, 607; Proc. Roy. Soc., 23, pp. 445, 473, 1875; 27, p. 439, 1878. Tomlinson, Proc. Roy. Soc. Lond., 42, p. 224, 1887; Beibl. 11, p. 659. Ewing, Beibl., 13, p. 186; Phil. Trans., 179, 333, 1888. Chree, Proc. Roy. Soc. Lond., 47, p. 41, 1899; Beibl., 14, p. 398; Phil. Trans., 181 A.

[4] Wien. Ber., 86, pp. 539, 550, 1882; Beibl. 7, p. 43, 1883.

The present experiment may be divided into two parts: (1) The investigation of the effect of different pressures upon each of the rings with a constant magnetizing force; and also the influence of residual magnetism upon the results. (2) The investigation of the effect of a certain pressure when magnetizing forces of different strengths are exerted upon the iron; and also of the variation of results with change in the condition of the iron.

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[1] Reference already given.

It was desired to avoid all end effects by the use of anchor rings, to secure higher pressure than the other experimenters had used and to test the effects with the same ring under various conditions and in different rings of the same material.

To obtain the pressure a special form of apparatus was designed (see Fig. 1) consisting of two parts of iron, 19 cm. outside diameter, with walls 6.2 cm. thick. The contact surfaces (*S*) were well ground and the iron ring (*R*) was placed within, then the two parts were joined by means of eight five-eighth-inch bolts, thus making a thick-walled compartment. The connection of wires was made by means of four metal plugs terminating on either side in binding posts (*B*)

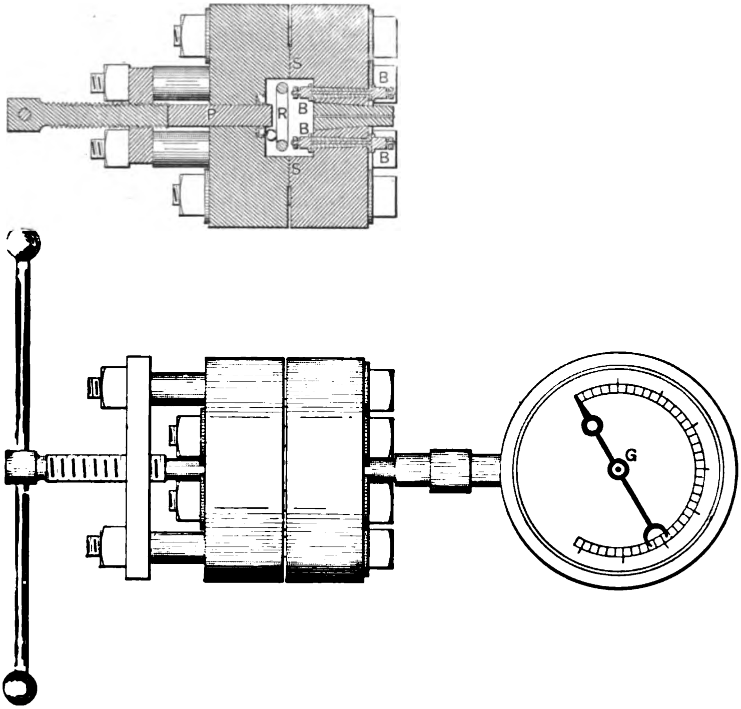

Fig. 1.

and insulated by taper plugs of hard rubber which passed through one end of the cylinder. A plunger in the other end was the means of obtaining pressure and the cavity was filled with oil through the hole for the plunger. Resin oil was used, which besides being very viscous is an excellent insulator. To avoid air bubbles the cylinder was first exhausted by an aspirator pump and the oil was then forced in by atmospheric pressure. A copper cap (*C*) prevented the leakage of oil around the plunger. Great difficulty was experienced in making the cylinders so tight that the desired pressure could be obtained without leakage. Various materials were tried between the halves but the tightest joint was finally secured by having the contact surfaces well ground. At first a slight smearing of vaseline and beeswax was used but later even this was found unnecessary. The pressure obtained was read directly from the gauge which registered as high as 18,000 lbs. per sq. in.

The three rings used were cut as nearly alike as possible from the same piece of Norway iron. They were wound with a secondary of No. 36 silk-covered copper wire, over which was a primary of No. 24 silk-covered copper wire. The layers were insulated from the iron and from one another by windings of insulating paper. Great care was exercised in winding that no wires should overlap. The dimensions and the data concerning the three rings used are given in the following table:

	Ring I.	Ring II.	Ring III.
Mean outer diameter.	5.46 cm.	5.41 cm.	4.45 cm.
Mean diameter of iron.	.624	.623	.661
No. turns in primary.	203	213	203
No. turns in secondary.	1,208	1,310	1,208

The galvanometer used was a D'Arsonval ballistic.

Part I. — Two rings were placed inside two pressure cylinders, so as to have both under the same conditions, and their primaries were connected in series with the desired number of cells of the storage battery, a resistance and an ammeter. The direction of throw of the galvanometer for each ring when the primary circuit was made or broken was noted; and the two secondaries were then connected in series with the galvanometer in such a way that the two throws opposed each other. It was then observed which coil was predominant in the effect and a series of readings was taken giving the throw for both make and break of the primary. The plunger of the cylinder was then pressed in by means of the screw until the desired amount was registered by the gauge and another series of readings was taken for the throw under the given pressure, after which a new set of zero pressure observations was recorded. The difference in the deflection of the galvanometer was an index of the change of induction due to the pressure exerted upon the iron core.

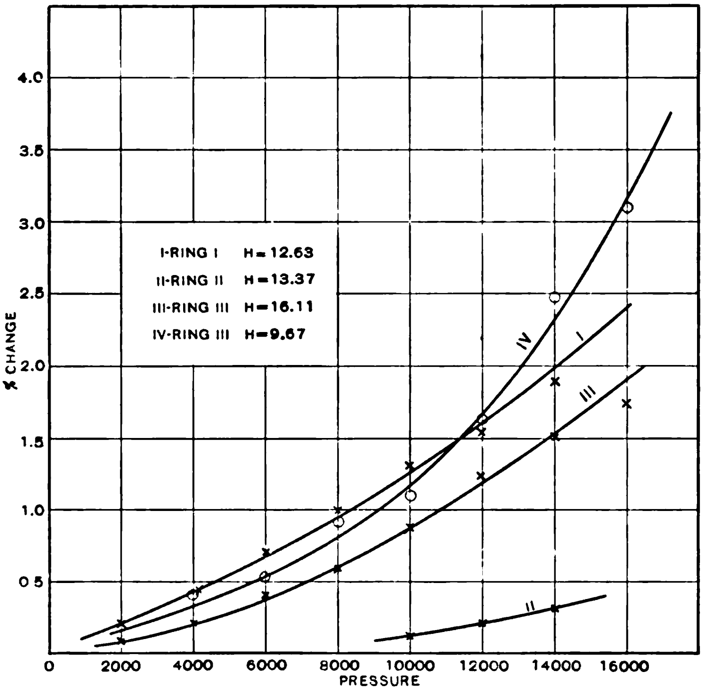

Fig. 2.

To ascertain the relative amount of this change the throw for each ring was observed when the same current was passed through the primary, and the secondary consisted of one or two turns; then the throw for the total number of turns, and the ratio of the change in induction to the total amount could be calculated.

In taking the readings it was found that the first throws after the pressure had been put on or removed were not in agreement with the later ones. This accords with Tomlinson's observation that part of the residual magnetism is lost when pressure is applied or removed. Before recording the deflections, the circuit was made and broken a sufficient number of times to secure a steady magnetic condition.

A correction must be made for the volume change due to the pressure. To make this the value for the modulus of elasticity of wrought iron ($= 25 \times 10^6$) given by Wm. Kent, Handbuch, p. 314, was assumed and the correction made before the curves were plotted.

In Fig. 2, curves I., II., III., are shown the curves of the three rings, which represent the means of results of readings taken on different days. It is seen from the curves that although the percentage of change varies with the different pieces of iron, the effect of pressure is of the same general character for the three rings; and with a magnetizing force of from 12 to 16 absolute units, the magnetic permeability of iron in this condition is increased by hydrostatic pressure.

The following is a table of the results plotted in Fig. 2, curves I., II. and III. Centimeters change in deflection and the percentage this change is of the total deflection are given, also the corrected value, taking account of the variation of volume with pressure. The pressure is expressed in pounds per square inch. The magnetizing force, *H*, is in absolute units.

	I. $H = 12.63$.			II. $H = 13.37$.			III. $H = 16.11$.		
Pressure.	**cm.**	**%**	**% cor.**	**cm.**	**%**	**% cor.**	**cm.**	**%**	**% cor.**
2,000	.18	.20	.21				.08	.09	.10
4,000	.36	.40	.42				.18	.20	.22
6,000	.62	.68	.70				.35	.39	.41
8,000	.86	.95	.98				.51	.56	.59
10,000	1.15	1.27	1.31	.08	.08	.12	.76	.84	.88
12,000	1.35	1.49	1.54	.18	.17	.22	1.07	1.18	1.23
14,000	1.68	1.84	1.90	.26	.25	.31	1.32	1.46	1.52
16,000							1.52	1.68	1.74

To be sure that the change in the amount of the throw was not due to any alteration of temperature caused by the pressure, the plunger was screwed in and the whole apparatus allowed to stand until any temperature difference would have been equalized by conduction, and the readings then taken agreed with the others.

The use of anchor rings made it possible to avoid end effects, but the method was open to the objection that the pressure was exerted upon the windings as well as upon the iron core itself, and it was necessary to be assured that the effect was not caused by this. A brass ring of the same dimensions as those of iron described above, and with similar windings on it, was subjected to the same treatment as the iron rings, but no change of deflection was observed. To test it in another way a balance of the throws was obtained by the insertion of an auxiliary solenoid, and then pressures of ten thousand and of fourteen thousand pounds were applied to the brass ring, and still no deflection of the galvanometer was observed. This showed that the change in deflection found before was not due to any changes produced in the windings or in the insulation by pressure.

Experiments proved that the position of the plunger within the ring had no effect upon the amount of throw, and that the number of layers of insulating paper between the successive layers of wire was immaterial, and also that the change in the compressed ring was independent of the opposing one and the second coil served only to cut down the deflection caused by the other so that the change could be observed.

It was known throughout the previous observations that the iron was probably almost saturated with magnetism, and for that reason one ring was carefully demagnetized by a gradually diminishing alternating current, and a new series of observations was made with a smaller value of H which would not give so near the maximum value of the intensity of magnetization. Great care was taken to keep the current steady as a slight change in the magnetizing force would cause a decided change in the magnetization. A change was also made in the method as the throw of the coil was diminished by resistance inserted in the secondary circuit instead of by means of a second coil. Each set of observations was taken with the current through the galvanometer first direct and then reversed. Curve IV., Fig. 2, shows the results obtained for ring III. after it had been demagnetized and treated in this manner, which shows that when the iron is not saturated with magnetism the percentage change is greater.

Results plotted in curve IV., Fig. 2, are given in the following table, where pressure is in pounds per square inch and the percentage change observed as well as the value corrected for volume change is recorded. Ring III. was used after demagnetization and $H = 9.67$.

Pressure.	Per cent. Change.	Per cent. Corrected.
4,000	.39	.41
6,000	.51	.53
8,000	.89	.92
10,000	1.06	1.10
12,000	1.58	1.63
14,000	2.42	2.48
16,000	3.05	3.11

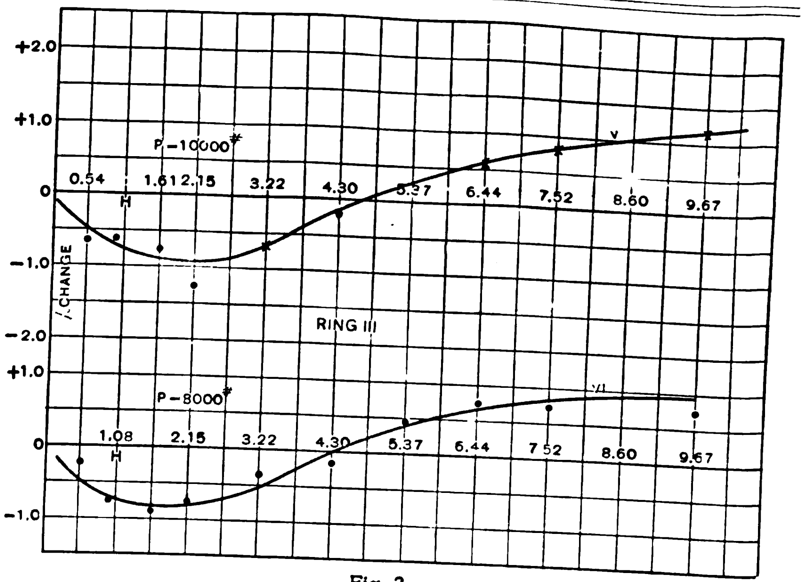

Fig. 3.

Part II. — As in the last observations of Part I. only one ring was used, and the deflection was cut down by the insertion of resistance in the secondary circuit. Instead of using the same current and taking the changes in deflection for various pressures, the current was varied for each set of readings and the pressure was each time made the same. The results are shown in Fig. 3, curves V. and VI. V. shows the percentage change of magnetic induction produced in ring III. by pressure of ten thousand pounds per square inch, when the magnetizing force varied from .54 to 9.67 c.g.s. units. VI. represents the effect of eight thousand pounds pressure for the same ring after demagnetization.

Table for Fig. 3. Curves V. and VI.; Current in Amperes and Values of H in Absolute Units.

Amperes.	*H*	**Curve V. 10,000 Pounds.**		**Curve VI. 8,000 Pounds.**	
		% Change.	**% Corrected.**	**% Change.**	**% Corrected.**
.025	.54	− .67	− .63	−.24	−.21
.045	.97	− .66	− .62	−.76	−.73
.075	1.61	− .77	− .73	−.90	−.87
.100	2.15	−1.31	−1.27	−.78	−.75
.150	3.22	− .71	− .67	−.36	−.33
.200	4.30	− .19	− .15	−.18	−.15
.250	5.37	+ .05	+ .09	+.41	+.44
.300	6.44	+ .56	+ .60	+.73	+.76
.350	7.52	+ .78	+ .82	+.69	+.72
.450	9.67	+1.11	+1.15	+.70	+.70

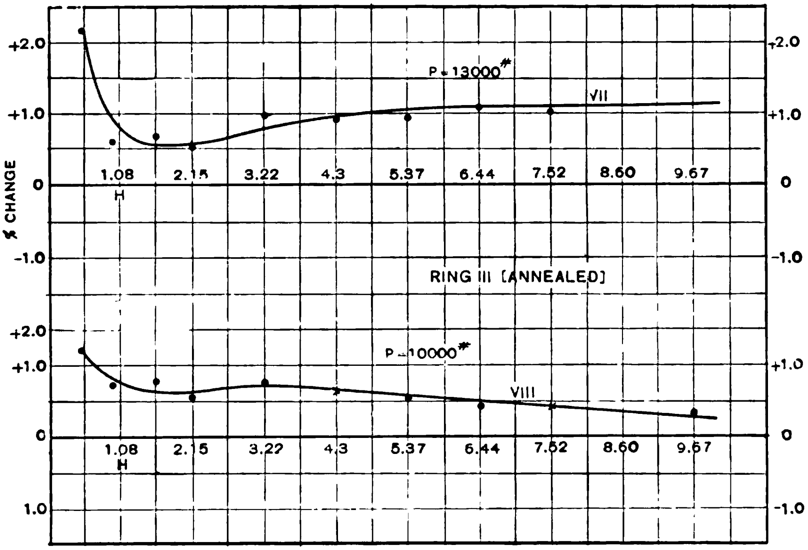

Fig. 4.

It is seen in both cases that with a small magnetizing force the magnetic induction decreases, reaching a minimum for a field whose strength lies between 1.6 and 2.1 absolute units. This diminution grows less with increasing fields, until for a value of *H* about 4.5 or 4.8 it shows a zero change. Further strengthening of the magnetizing field results in an increase, which seems to approach a maximum for *H* equal to approximately 9 c.g.s. units with eight thousand pounds pressure, and for a slightly larger value when the pressure is ten thousand pounds.

After the ring had been very carefully annealed another series of observations gave the results represented in curves VII. and VIII., Fig. 4. For VII., as the iron had just been annealed, there was no need of demagnetization; the pressure applied was thirteen thousand pounds per square inch. Before the readings for VIII. were taken the ring was demagnetized; the pressure in this case was ten thousand pounds. The table of results plotted is the following:

Amperes.	*H*	**Curve VII. 13,000 Pounds.**		**Curve VIII. 10,000 Pounds.**	
		% Change.	**% Corrected.**	**% Change.**	**% Corrected.**
.025	.54	+2.10	+2.15	+1.14	+1.18
.045	.97	.54	.59	.68	.72
.075	1.61	.64	.69	.74	.78
.100	2.15	.46	.51	.55	.59
.150	3.22	.94	.99	.70	.74
.200	4.30	.89	.94	.63	.67
.250	5.37	.90	.95	.51	.55
.300	6.44	1.05	1.10	.37	.41
.350	7.52	.97	1.02	.37	.41
.450	9.67			.32	.36

It is interesting to note on comparison of these values with those obtained for the same ring before it was annealed, that in this case the change is an increase for every value of *H* used, and that, with the exception of the first value which was obtained with a very small current, the percentages of change are included within narrower limits for the annealed iron. It is seen that the second, third and fourth points of the curve seem to give a slight wave, but it was felt that the results were hardly sufficiently accurate to warrant drawing it in. Curiously the effect of ten thousand pounds pressure diminishes for greater strengths of the field.

Throughout the observations great care was taken to keep the conditions steady. The current was watched carefully, and was maintained at the desired value by a slight alteration of the resistance in the primary circuit. The pressure was kept as constant as possible during the time required for the observations.

The experiment seems to warrant the following conclusions:

1. The application of hydrostatic pressure to soft iron anchor rings changes the coefficient of magnetic permeability of the iron, besides altering the amount of residual magnetism when the pressure is applied or removed. The amount of the change varies for different pieces of iron.

2. With unannealed iron the sign of the change depends upon the strength of the magnetizing field; the effect in small fields being a decrease, and in stronger fields an increase; the change of sign occurs for $H = 4.5$ or 5 c.g.s. units. The magnitude of the alteration is a function of both field and pressure.

3. With annealed iron an increase is found for pressure with all values of field between .54 and 9.67 absolute units.

The results with the unnealed iron are in agreement with those obtained by Wassmuth in his experiment, as there is a decrease and then an increase for values of H approaching the maximum of magnetization. But for the values of the field used by Nagaoka and Honda there is clearly an increase for iron, annealed and unannealed whereas they obtained only a decrease in magnetization, which was not the result called for by Kirchoff's theory and their own experiments on other forms of magnetostriction. The results of this investigation would then tend to support the theory of magnetism advanced by Kirchoff for annealed soft iron.

The author wishes to express her indebtedness to Professor Michelson, of the University of Chicago, for suggesting the problem, and the method of attack, and for his aid throughout the investigation; to Professors Mann and Millikan for their encouragement and assistance during the work; and to Dr. Jewett who assisted in taking the final observations, and made the drawings for this article.

BARNARD COLLEGE.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE TWENTY-FOURTH MEETING.

THE spring meeting of the Physical Society was held at the Cosmos Club, Washington, D. C., on Friday, April 22, and Saturday, April 23, 1904.

The following papers were presented:

1. A Study of the Silver Voltameter. K. E. GUTHE.
2. Some new Rectifying Effects in Conducting Gases. P. G. NUTTING.
3. The Effect of Light on the Absorption and Electrical Conductivity of Fluorescent Liquids. E. L. NICHOLS and ERNEST MERRITT.
4. Some Additions to the Arc Spectra of the Alkali Metals. F. A. SAUNDERS.
5. The Volumes of Solutions. W. F. MAGIE.
6. Absolute Electrodynamometers. G. W. PATTERSON.
7. Induced Radioactivity due to Radium. E. P. ADAMS.
8. The Energy Density, the Tension, and the Pressure in a Magnetic Field. (Read by title.) S. J. BARNETT.
9. A Recomparison of the U. S. Prototype Meter at the International Bureau of Weights and Measures. L. A. FISCHER.
10. (*a*) High Temperature Measurement by means of Optical Pyrometers. (*b*) Note on Special Problems in Optical Pyrometry. C. W. WAIDNER and G. K. BURGESS.
11. Apparatus for Platinum Resistance Thermometry. C. W. WAIDNER and H. C. DICKINSON.
12. Intercomparison of Primary Standard Mercurial Thermometers. C. W. WAIDNER and H. C. DICKINSON.
13. The Standard Cell. F. A. WOLFF.
14. The Peculiar Behavior of Some Resistance Standards and Its Explanation. F. A. WOLFF.
15. A Direct Reading Apparatus for the Calibration of Resistance Boxes. F. A. WOLFF.

16. Absolute Measurement of Capacity. E. B. ROSA and F. W. GROVER.

17. Absolute Measurement of Inductance. E. B. ROSA and F. W. GROVER.

18. The Testing of Mica Condensers. E. B. ROSA and F. W. GROVER.

19. Testing of Alternating-Current Instruments. (Read by title.) E. B. ROSA and M. G. LLOYD.

20. Equilibrium of Vapor Pressure over Curved Surfaces. (Read by title.) A. A. BACON.

Adjourned at 1 P. M., April 23.

E. B. ROSA,
Secretary pro tempore.

A STUDY OF THE SILVER VOLTAMETER.[1]

BY K. E. GUTHE.

THE unsatisfactory results obtained with the common type of silver voltameter have led to the impression that this instrument cannot be regarded as very reliable. Recently Richards with his students and Leduc have attempted to improve the instrument, and claim to have obtained a high degree of accuracy. The present investigation was undertaken in order to compare different forms and subject them to a severe test.

Richards has pointed out that the main trouble arises from the formation of a complex ion at the anode which, when transported to the kathode, will deposit too much silver. To prevent the anode liquid from reaching the kathode, he surrounds the anode, consisting of a silver rod, by a porous, fine-grained cup and keeps the level of the electrolyte in this cup always lower than that of the outside. Leduc, on the other hand, hopes to prevent the formation of the disturbing ion by using a very small current density at the anode, and he therefore employs as anode a mass of granulated silver surrounded by filter paper.

The experiments described show (1) that the usual type of silver voltameter is not a very reliable instrument for measuring quantity of electricity; (2) that Leduc's type does not prevent the formation of the complex ion, even with small anode current density; (3) that the use of filter paper must be avoided in the silver voltameter; (4) that silver in contact with the anode liquid breaks up the complex ion.

The Richards type is the only satisfactory form so far proposed and gives very constant results. For convenience in manipulation this type has been modified in such a way as to avoid the necessity of removing, by frequent pipetting, the anode liquid from the bottom of the porous cups. Finely divided silver was placed at the bottom of the cup and this effectually removed the complex ion. In order to insure a constant resistance of the voltameter it was found necessary to surround the lower part of the porous cup by a small glass beaker.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22, 1904.

A second type proposed by the author is the large silver anode voltameter. Granulated silver is placed in a layer about 0.5 cm. deep at the bottom of a large porous cup; upon this is pressed the silver plate forming the anode connection. The whole is immersed into the platinum bowl (the kathode) containing neutral 20 per cent. solution of silver nitrate.

To test the degree of accuracy which may be obtained with these voltameters in a number of independent experiments, the instruments were arranged in series with a standard resistance, and the current adjusted so as to give a terminal potential difference equal to the E.M.F. of a Weston cell, which was used throughout the investigation. In the different experiments resistance standards of 5, 2, and 1 ohm were used, and in one case a 2 and a 1 ohm placed in parallel, so that currents ranging from 0.2 to 1.5 amperes were employed. In all experiments a little more than 4 grams of silver was deposited at the kathode.

The results obtained with the Richards type and the two designed by the author were very consistent, the largest variation of any single value from the mean not exceeding 1 in 20,000, except when a current of only 0.2 amperes was used. The experiments in this case lasted five hours and the deposits became too heavy due on account of diffusion of the anode liquid through the cups. In the experiments lasting a shorter time no such difficulty was experienced.

The electrochemical equivalent of silver, expressed in terms of the present standards of the Bureau—assuming that the Clark cell has an E.M.F. of 1.434 volts at 15°C., according to the legal specifications — was found to be by—

The Richards type	1.11682 mg. per coulomb.
The modified Richards type	1.11682 " " "
The large Anode type	1.11683 " " "

Relative comparison with other forms gave for the usual type 0.048 per cent., for the Ag_2O type, employed by Patterson and Guthe 0.058 per cent. larger deposits.

This would increase the electrochemical equivalent of silver as determined by means of the former to 1.11736, and for the Ag_2O voltameter to 1.11747 mg. per coulomb; this agrees well with the results of Kahle, who calculated, taking the electrochemical equivalent as 1.118 mg., the E.M.F. of the Clark cell to 1.43305 volt. On the basis stated above the electrochemical equivalent would be reduced to 1.11726 mg.

It seems highly desirable that in future experiments, especially in absolute measurements of current, the type now in common use be abandoned. Any one of the three forms mentioned above will allow a degree of accuracy which cannot be obtained by the other method.

Bureau of Standards,
Washington, D. C.

The Effect of Light Upon the Absorption and the Electrical Conductivity of Fluorescent Solutions.[1]

By E. L. Nichols and Ernest Merritt.

It is a general characteristic of fluorescent bodies that the light emitted during fluorescence is different in color from the light which the body absorbs, and to which the fluorescence is due. Although the absorption spectrum and the fluorescence spectrum overlap they do not coincide. In fact the fluorescence spectrum often extends to wave-lengths for which the absorption of the substance, as ordinarily measured, is practically *nil*. Since we are accustomed to the view that absorption and emission are converse phenomena, and that under like conditions a substance absorbs the same rays that it is capable of emitting, it is therefore natural to expect that the absorbing power of a fluorescent body will be modified by fluorescence.

Such an effect has, in fact, been observed by Burke,[2] who found that the absorption of uranium glass was about 30 per cent. greater when the glass was brightly fluorescent than when its absorption was determined under ordinary conditions. The light used in Burke's experiments was that due to the fluorescence of a second piece of uranium glass.

The writers have recently investigated the influence of fluorescence upon absorption in the case of a solution of fluoresceïn. Measurements were made by means of a Lummer-Brodhun spectro-photometer for a number of different wave-lengths throughout the region in which the effect was observable. Upon plotting the results it was found that the effect of fluorescence is to introduce a new and well-defined band into the absorption spectrum of the solution, the extent of this band being approximately that of the spectrum of the fluorescent light. In the case of a rather dilute solution the maximum increase in absorption occurred at wave-length .507 μ. When fluorescence was excited by a group of four acetylene burners the increase in absorption at this point amounted to 67 per cent. In a more concentrated solution the region of greatest increase in absorption lies further toward the red, and coincides closely with the edge of the normal absorption band. The percentage absorption due to fluorescence was found to be a function of the intensity of the incident light, being greatest when the intensity of the incident light was least.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22, 1904.

[2] Philosophical Transactions, Vol. 191 (A), p. 87, 1898.

The action of light upon a fluorescent substance thus produces a distinct change in its behavior. It appears to us not unlikely that this change is to be ascribed to some type of temporary dissociation brought about by the exciting light. If this view is correct fluorescence might result from the violent oscillations that would probably occur, not only at the instant of dissociation, but also during the subsequent recombination. A temporary change in the absorbing power of the substance would also be expected. From the standpoint of the electromagnetic theory of light a type of dissociation which results in splitting up the molecule into positive and negative ions seems not only possible but probable, especially in the case of substances possessing well-marked absorption bands. Such a dissociation might be of the ordinary electrolytic type, or it might be similar to that which occurs in gases under the influence of Roentgen rays. In either case it would produce an increase in electrical conductivity.

We have investigated the effect of fluorescence upon conducting power in the case of five fluorescent solutions, each of which shows a small but perfectly definite increase in conductivity when illuminated. During the test the solutions were contained in a glass cell whose parallel vertical sides were about 0.1 mm. apart. The electrodes were pieces of platinum foil about 20 mm. long. They were mounted vertically and were approximately 2 mm. apart. In order to make the normal conducting power small, absolute alcohol was used as a solvent. The solutions were made so concentrated that the fluorescence was confined to a thin layer at the surface. Under these conditions the normal resistance of the cell, without illumination, ranged from 1,000,000 ohms in the case of fluorescein to 90,000 ohms in the case of fuchsin. The electric arc was used as a source of light. Direct illumination of the cell by the undispersed rays of the arc could not be employed on account of the heating effect; even when the rays were passed through a water bath the change in resistance due to rise in temperature was considerably greater than that due to fluorescence. The solution to be tested was therefore placed in the spectrum of the arc, and no further disturbance due to temperature effects was experienced. No change in resistance was observed except when the rays falling on the solution were capable of producing fluorescence; and the maximum increase in conductivity occurred in the region where the fluorescence was brightest. For the different substances tested the observed increase in conductivity had the following values: Eosin, 1.1 per cent.; fluorescein, 0.11 per cent.; rhodamin, 0.14 per cent ; naphthalin roth, 0.06 per cent.; cyanin, 0.59 per cent. In the case of an alcoholic solution of fuchsin, which was not fluorescent, no change in resistance was observed, although the conditions were such that a change of .008 per cent. could have been detected.

THE VOLUMES OF SOLUTIONS.[1]

BY WILLIAM FRANCIS MAGIE.

WHEN a solution is made by dissolving a salt or some other electrolyte in water, the volume of the solution is always less than the sum of the volumes of the water and of the solid which was dissolved. There are cases in which the volume of the solution is less than that of the water which enters into it. In such cases certainly a condensation of some or all of the water must occur. We may conceive of the volume of the solution as made up of three parts ; (1) the volume of that portion of the water which is not within the sphere of influence of the solute, or which is not associated with it ; (2) the volume of the undissociated molecules of the solute and of the water associated with them ; (3) the volume of the dissociated ions of the solute and of the water associated with them. From this conception it follows that the volume of the solution may be represented by the formula

$$V = W + A(n - p) + Cp,$$

in which W represents the volume of the water used ; n, the number of gram-molecules of solute ; p, the number of these gram-molecules which are dissociated (in case $n = 1$, p represents the dissociation factor) ; and A and C are quantities which depend respectively on the undissociated molecules of the solute, and on the dissociated ions. The formula is most conveniently tested by setting $n = 1$, $C - A = B$, and using $V = W + A + Bp$. Comparison with the experimental data shows that for each solute A and B are constants over a considerable range of dilution.

A formula of this form has been applied by MacGregor[1] to the density of solutions. The density, however, is not an additive property, and the constants obtained do not admit of interpretation. On the other hand, we may fairly assume that, so long as the solution is so dilute that a considerable portion of the water is outside the range of action of the solute, the volume of the solution is strictly an additive property.

Others of MacGregor's results are obtained by the use of the formula on additive properties, and confirm the conception of a solution held in this paper.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22, 1904.

[2] Phil. Mag., Jan.-June, 1897.

From the data given by MacGregor for the density of sodium chloride solutions we may calculate the amount of water present in the solutions of various strengths, and also the constants A and B. The results obtained when the formula is used to calculate the volumes of the different solutions are exhibited in the following table. In this table the column headed n contains the number of gram-molecules of sodium chloride in one liter of solution. The column headed V contains the calculated volumes of the solutions, which, by experiment, should be uniformly 1,000 c.c.

Sodium Chloride.

$A = 26.06$, $B = -12$.		$A = 26.06$, $B = -12$.	
n	V	n	V
0.25	999.89	1.5	999.55
0.50	1,000.04	2.0	1,000.08
1.00	1,000.00	2.5	999.99

The volume of one gram-molecule of solid sodium chloride ranges, according to the various determinations of the density, between 26 and 27. The value of A is therefore equal to the molecular volume of the solid salt. and we may conclude that the volume of the undissociated molecule of salt is not changed on solution, and that, if the molecule of salt is associated with molecules of water their volume is not changed thereby.

Calculations on data furnished by Kohlrausch and Hallwachs[1] confirm the validity of the formula in a similar manner. In most cases the calculated results obtained depart from the observations when the value of n is greater than 1.

Thomsen[2] furnished data expressed in a different way, by which also the validity of the formula may be illustrated. In the following tables the column headed N contains the number of gram-molecules of water used to dissolve one gram-molecule of the solute. The column headed p contains the dissociation factor, obtained from Kohlrausch's tables of conductivity. The other columns contain the observed volumes of these solutions and the volumes calculated with the formula.

Sodium Hydroxide.

$A = 7$, $B = -15$.			
N	p	Obs.	Calc.
30	0.602	537.9	538.0
50	.696	896.4	897.0
100	.775	1,795.9	1,795.4
200	.824	3,594.8	3,594.7

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[1] Wied. Ann., 50, 1893.

[2] Thermochemische Untersuchungen, vol. 1.

The molecular volume of solid sodium hydroxide is 19, greater than the value of *A*. There appears to be a considerable shrinkage either of the undissociated molecule or of water molecules associated with it.

Ammonium Chloride.

$A = 43.5$, $B = -7.5$.			
N	p	Obs.	Calc.
10	0.593	219.0	219.1
25	.703	488.2	488.2
50	.742	937.8	937.9
100	.777	1,837.7	1,837.7
200	.806	3,637.6	3,637.5

The molecular volume of the solid ammonium chloride is 35, less than the value of *A*. The molecule appears to increase in volume on solution or to affect the associated water molecules so as to increase their volume.

Similar calculations on other data given by Thomsen confirm the validity of the formula in a similar manner.

The constant $C = A + B$ of the formula depends on the dissociated ions of the solute and on the water associated with them. In case the solute is one which divides into two ions, this constant is the sum of two similar constants, C_0 and C_1, which depend respectively on the two ions. If, now, we know the values of C for two solutes which have a common ion, and if the constant C_0 depending on this common ion has the same value in both solutions then the difference of the values of C for the two solutions, or $C_1 - C^2$, will depend only on the other two ions, and will be the same for any pair of compounds of those two ions with a common ion. This conclusion from the hypothesis is illustrated by the results contained in the following table, in which are given the values of C for three pairs of compounds of potassium and sodium with common ions. The differences of the values of C for each pair are very nearly equal.

Values of C and Differences.

KCl	23	KOH	1	KNO_3	35.5
NaCl	14	NaOH	−8	$NaNO_3$	24.4
Difference,	9		9		11.0

It has been shown[1] that a formula of the same form as the one illustrated here applies to the heat capacities of solutions. Since the heat capacity is also manifestly an additive property of a composite body, this serves to confirm the conception of the nature of a solution from which the formula was deduced. The results in general also con-

[1] Bull. Am. Phys. Soc., vol. 2, no. 2.

firm the correctness of the dissociation factors obtained by the measurement of conductivity.

It is very desirable to obtain a set of tables of conductivities, or of the corresponding dissociation factors, for solutions made up by adding one gram-molecule of the solute to a known number of gram-molecules of the solvent. The theoretical formulas which apply to solutions imply the use of such solutions, and the illustration of those formulas by the data which exist at the present time involves tedious and somewhat uncertain calculations. Such tables would be far more convenient for the use of the physicist than those in which the strength of the solutions is given in gram-molecules per liter.

THE ENERGY DENSITY, TENSION AND PRESSURE IN A MAGNETIC FIELD.[1]

BY S. J. BARNETT.

THE general expression for the magnetic energy density at a point at which the induction is proportional to the intensity is obtained by equating the volume integral of the energy density in the field of a simple circuit in a medium in which the induction is everywhere proportional to the intensity to half the product of the current in the circuit (expressed as $\frac{1}{4}\pi$ times the line integral of the magnetic intensity around it) and the magnetic flux through the circuit, and comparing the two expressions.

The expressions for the magnetic tension and pressure at a point at which the induction and intensity are proportional and parallel are simply and rigorously obtained by the application to simple circuits of Maxwell's relations between the change in the electrokinetic energy of a system, with constant fluxes or constant currents, and the work done by the electromagnetic forces when the system undergoes an infinitesimal change of configuration. The magnetic pressure is also deduced from Ampère's law.

SOME ADDITIONS TO THE ARC SPECTRA OF THE ALKALI METALS.[1]

BY F. A. SAUNDERS.

LENARD[2] discovered by means of a slitless spectroscope a new series and several other lines in the spectrum of sodium. The object of the present investigation was to see if these could not be found by ordinary methods if the apparatus gave spectra free from astigmatism and with sufficient economy of light. A Rowland concave grating was used, of 10 cm. width and 305 cm. radius, ruled with unusually long lines on a parabolic surface. The light from the slit was rendered parallel before reaching the grating by falling on a 10 cm. parabolic mirror. The spectra were formed 150 cm. from the grating, along a curve which is nearly a circle of 75 cm. radius; they were free from astigmatism, at least in part, and were, when photographed on a film of suitable curvature, of very good definition over a space of 25 cm., corresponding to about 2,700 tenth-meters in the first order.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22, 1904.

[2] Ann. d. Ph., 11, p. 636, 1903.

The purchase of this apparatus was made possible by the generosity of the Rumford Fund Committee.

Photographs were obtained showing Lenard's new series in the sodium spectrum and one or two new lines not mentioned by Lenard. The series lines could be seen as pairs of diffuse lines, the stronger line having the greater wave-length. Careful measurements were taken of the wave-lengths of these lines. Two new terms were added to the series; one in the deep red (taken by a three-hour exposure on a film stained with cyanin) and another in the blue. The series pairs have constant wave-number differences, the separation being about 0.85 that of the subordinate series. No formula has as yet been found to fit the series unless it has four arbitrary constants; those of Kayser and Runge, Rydberg, Fowler and Ritz were tried, along with others, modifications of these.

Two new lines have been found in the spectrum of lithium, which when combined with the line at 4,636 measured by Hagenbach[1] form a new series, also apparently of the subordinate type. Its lines accompany those of the first subordinate series, perhaps as "satellites" though their separation from the parent lines is considerable. They are diffuse and broadened toward the red. The lithium lines near 4,602 appear to admit of a different interpretation from that given by Hagenbach. It seems easiest to explain them as consisting of one line at 4,603.2, broadened toward the red, which is a member of the first subordinate series, and a line at 4,601.6, broadened toward the violet, analogous to the pair in the sodium spectrum at 5,676 and 5,670.

In the spectrum of potassium one new line has been found, predicted by Ritz,[2] in almost exactly the predicted place (6,964.7). It is one of the hitherto missing first pair of the first subordinate series, which is, for some obscure reason, very faint. The other member of this pair was not found, owing to the broadening of the line at 6,938.8 near which it doubtless lies.

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[1] Ann. d. Ph., 9, p. 48, 1902.

[2] Ann. d. Ph., 12, p. 264, 1903.

Two new lines were found in the spectrum of rubidium; one a principal series line at 3,158.7 (not seen as a pair) and a very diffuse and faint line at 5,171, which with 5,234.6[1] forms a pair in the second subordinate series. No other new lines were found though the spectrum was well photographed down to 8,000 *t-m.*

In the cæsium spectrum five new lines were found, one at 7,944.7, a member of the second subordinate series, predicted by Ritz, and the others members of pairs of lines with constant wave-number differences, which, combined with lines previously observed and not belonging to the regular series, form two new series of the subordinate type, running to the same end. This end is not, however, the end of the regular series also, but is somewhat nearer the red. These lines are so exceedingly diffuse that their positions cannot be measured with much accuracy. It seems most unlikely from their appearance that they can be due to any impurity. It does not appear to have been previously noticed that the heavier line of each pair in the first subordinate series is accompanied by a companion (lines all observed by Ramage) on the red side, forming a "secondary" series.

In all the above spectra several lines in the deepest red were carefully measured whenever it seemed that the existing measurements could be improved upon. The results differ considerably from those of Lehmann,[2] in some cases by several tenth-meters. Special precautions were taken to avoid errorrs and check measurements and it is thought that in this case the "probable" error and the "possible" error are neither more than a few tenths of a tenth-meter.

THE STANDARD CELL.[3]

By F. A. Wolff, Jr.

In the paper is briefly discussed the main proposition, which will be taken up by the Chamber of Delegates in the St. Louis International Electrical Congress — the redefinition of the fundamental international electrical units.

At the Chicago Congress the ohm was defined in terms of the resistance of a column of mercury of specified length and mass and at a specified temperature; the ampere as a one tenth of a C.G.S. electro-magnetic unit and as being represented sufficiently well by a current which deposits silver at a specified rate under specified conditions; the volt in terms of the ohm and ampere and as being defined sufficiently well in terms of the Clark standard cell, assuming for the electromotive force of the latter at 15° Centigrade the value of 1.434 volts.

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[1] Observed by Ramage, Astrophys. Jour., 16, p. 43, 1902.

[2] Ann. d. Ph., 5, p. 638, 1901.

[3] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22, 1904.

While it was supposed that these definitions would serve as the basis for legislative enactment by the various countries represented, few have taken definite action and nearly all have adopted definitions not in strict accord with the above. This may be attributed to the following reasons:

All three of the fundamental units are defined in terms of concrete standards, notwithstanding that they are connected by Ohm's law.

The specifications for the silver voltameter were shown to be entirely inadequate.

The assumed value for the electromotive force of the Clark cell was shown to be too high by about 1 in 1,400.

The application of potentiometer methods and the improvement in the methods for measurement of low resistance standards have set a standard of accuracy for relative measurements of current and electromotive force far in excess of that fixed by the reproducibility of the fundamental standards.

The St. Louis Congress will therefore most likely be called upon to define two of the three fundamental electrical units in terms of concrete standards, in which case the third will be defined in terms of the other two. The definition of the ohm is almost free from criticism, and the choice for the second unit lies between the ampere defined in terms of the electrochemical equivalent of silver and the volt as defined in terms of the electromotive force of some standard cell. The great superiority of the Weston cadmium cell over the Clark cell would seem to point to the entire displacement of the latter. The arguments for and against both propositions are reviewed, the deciding argument in favor of the adoption of the standard cell being the necessity of using the same as a working standard at least in actual practice, owing to the limited range of application of the silver voltameter, even if the reproducibility of the cell should be somewhat less than the accuracy of silver voltameter determinations. As the reproducibility of the cell depends upon the purity of the materials employed and principally upon the mercurous sulphate, an electrolytic method for the preparation of the latter material was devised, consisting in the electrolysis of a five per cent. sulphuric acid solution between mercury electrodes, the solution and the mercury anode being agitated by means of a glass stirrer. (Practically the same method was described independently by Carhart and Hulett and by the author at the annual meeting of the Electrochemical Society on April 7, 1904.)

Experiments with Weston cells set up from this material and with single electrode cells showed that the electrolytically prepared material gave a constant electromotive force to within one or two parts in 100,000 and values about two tenths millivolts less than the best commercial samples of chemically pure mercurous sulphate washed with water in accordance with the Chicago specifications. This difference was shown to be due to the basic mercurous sulphate, either in the samples or produced by the action of the water, as the same samples when treated with ten per cent. sulphuric acid and washed with concentrated neutralized cadmium sulphate solution gave values almost in agreement with those obtained from the electrolytic material. In addition, samples of electrolytic mercurous sulphate treated with water, thus rendering it basic, gave values about two tenths millivolts higher than when the sample was washed directly with concentrated neutralized cadmium sulphate solution. The cells prepared with the new material seemed to come to a state of equilibrium immediately after setting up, which, as is well known, is not the case with the cells prepared from commercial materials, all of which contain at least traces of basic mercuric sulphate. This may be attributed to the presence of this material, which is slowly reduced in the cell and which is also removed by washing with ten per cent. sulphuric acid, and which if added to the electrolytic mercurous sulphate gives values considerably in excess of the normal values.

A Direct Reading Apparatus for Calibrating Resistance Boxes.[1]

By F. A. Wolff, Jr.

IN precision comparisons of the coils of resistance boxes, the variable plug and other contact resistances introduce serious errors unless special methods involving a determination of such connecting resistances or their elimination are employed.

The method described by the author consists of determining the relative values of the coils belonging to a decade or to adjacent decades by shunting these coils in series with each other by a series of 100-ohm coils, the galvanometer being connected in turn across corresponding points of the two series. The apparatus is made direct reading by applying a Kelvin-Varley shunt to four adjacent coils of the auxiliary series, the shunt having a resistance of 400 ohms and including in its middle portion a bridge wire having a range of ± 1 per cent.

The relative values of the coils are given by the differences in the readings obtained, and it is therefore only necessary to determine the value of one of the coils of the series, to determine the values of all in international ohms. The method is applicable to boxes in which the coils may be put in series and in which a galvanometer contact may be applied to the contact blocks to which the coils are attached. In the series plug rheostats this may be accomphished by means of a split plug, one half of which is composed of insulating material.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22, 1904.

THE PECULIAR BEHAVIOR OF SOME RESISTANCE STANDARDS AND ITS EXPLANATION.

By F. A. Wolff, Jr.

SOME years ago it was noticed by Professor T. C. Mendenhall and by Professor Benjamin F. Thomas, that certain paraffin insulated resistance coils showed polarization effects due to the application of the test current. The same behavior is noticed occasionally, even with coils insulated by shellacing and subsequent baking, and is to be attributed to an electrolytic shunt, the polarization of which causes an apparent increase in the resistance as the test current is left on. On the reversal of the test current the resistance is apparently too low, but gradually increases to its former value. The effect is produced by dipping a coil which does not show the effect in water and is eliminated by subsequent baking.

Another effect, which has not been described before, manifests itself by a decrease in resistance as the test current is left on, the amount of decrease depending upon the voltage applied to the coil. The variation is irreversible, depending upon the previous currents and their direction, and the behavior is exactly similar to that of a coherer resistance. The effect cannot be accounted for by thermal or voltaic electromotive forces, and probably consists of a coherer shunt to a portion of the coil, due to a metal filing imbedded in the shellac between turns. As Branly has shown, such coherer effects may be obtained even with solid dielectrics.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22, 1904.

NEW BOOKS.

The Induction Motor, Its Theory and Design Set Forth by a Practical Method of Calculation. By Henri Boy de La Tour. Translated from the French by C. O. Mailloux. McGraw Publishing Co., New York, 1903. Pp. 1 + 200.

This admirable book comprises a most thorough analysis of the induction motor. The graphical and mathematical treatment is concrete and is made practical by application to numerical cases. It is well adopted to the uses of designing engineers and engineering students.

The translator, while respecting the individuality and originality of the author, has shown considerable interest in making the English presentation of the subject as good as possible. He is to be commended for his careful use of terms, for the introduction of "torque" (contrary to the general custom of continental writers) and for the use of the "maxwell" and the "gauss" as units of magnetic flux and density. We look askance at the statement: "The terms *watted power* and *wattless power* are self explanatory." Both author and translator show themselves to be strong believers in the induction motor. Both are to be congratulated for this comprehensive presentation of the subject.

F. Bedell.

Conductors for Electrical Distribution; their Materials and Manufacture, The Calculation of Circuits; Pole-Line Construction, Underground Working, and other Uses. By F. A. C. Perrine. D. Van Nostrand Company, New York, 1903. Pp. 1 + 280.

In this volume the subject of electrical conductors is treated from two aspects, that of manufacture and that of engineering, two aspects so distinct that we would criticise the bringing of the two together were it not for the fact that the author is peculiarly fitted to treat of each.

About half the book deals with the art of wire making. Here is a fund of information which the author's experience as manufacturer makes authoritative.

The remaining half deals with engineering and here too the stamp of the writer is shown. Well known work, as Kelvin's law of economy of conductors is clearly treated. The chapters on line calculations form the most valuable part of the book. The method of treatment first given by Perrine and Baum before the American Institute of Electrical Engineers in 1900 is given in full. This treatment, which is practically correct, is much simpler than that previously given by various writers on the theory of lines with distributed self-induction and capacity.

The book is commended to the student and the transmission-line engineer.

F. BEDELL.

Engineering Preliminaries for an Interurban Electric Railway. By ERNEST GONZENBACH. McGraw Publishing Co., New York, 1903. Pp. 1 + 71.

This is a brief report on a proposed railway in the Middle West. The author states that it is not to be construed as an attempt to generalize, but it is intended to show the way in which certain conditions were to be met in a certain case. The field of the book is obviously limited.

F. B.

Notes on Electric Railway Economics and Preliminary Engineering. By W. C. GOTSHALL. McGraw Publishing Co., New York, 1903. Pp. 1 + 248.

The author expresses his intention to consider his subject broadly and as a whole, to outline the work of the electric railway engineer during the inaugurative and constructive period of a proposed road, and to give in a general way some bases upon which the costs of construction, probable traffic and ultimate economic results of the proposed railway can be guaged. The analysis of the subject is well made and the treatment clear.

F. B.

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